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Catalytic Conversion of Hazardous and Toxic Chemicals: Catalytic Hydrodechlorination of Polychlorinated Pesticides and Related Substances

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This research was supported by the EPA so that more effective ways can be found to detoxify unwanted hazardous wastes.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

ABSTRACT

A study has been undertaken of the catalytic conversion of chlorinated pesticides and other environmentally undesirable chlorinated materials into acceptable compounds. The results of this study show that chlorine can be catalytically removed and replaced by hydrogen to produce relatively nontoxic hydrocarbons which may either be useful as items of commerce or which may be easily combusted.

The experimental foundation for a large scale hydrodechlorination process has been laid. The Process involves the use of a supported nickel catalyst in a batch process using ethanol as a solvent and sodium hydroxide as an acid acceptor of the hydrogen chloride byproduct. Temperatures of less than 150°C and hydrogen pressures of less than 50 atmospheres are required for most classes of chlorinated pesticides and related substances. Palladium as a catalyst did not give results which were significantly better than nickel.

A reactivity sequence has been established based on carbon chlorine bonding, wherein olefinic chlorine is most reactive, aromatic chlorine is less reactive and aliphatic chlorine is least reactive.

Reaction models have been proposed and the relative rates of parallel and consecutive hydrodechlorination steps have been determined for Aroclor and DDE under various process conditions.

Removal of ortho substituted chlorine is the limiting reaction in hydrodechlorination of Polychlorinated Biphenyls (PCB's). Highly bridged and nonplanar molecules such as Aldrin and Dieldrin are the most difficult compounds to hydrodechlorinate due to steric effects. Removal of aromatic chlorine is the limiting reactor in the hydrodechlorination of DDT and DDE.

The hydrodechlorination process as described should be applicable to other classes of pesticides such as the isomeric hexachlorocyclohexanes (e.g., Lindane), and the Methanoindenes (e.g., Chlordane). Due to steric effects chlordane should have a reactivity similar to that of Aldrin.

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I INTRODUCTION

Many of the widely used insecticides and other organic chemicals which have been found to persist in the environment and in the food chain are chlorinated compounds. These compounds, like DDT, have been found to have a very long life and to remain unchanged both in the environment in general and in the fatty tissues of fish, birds and animals.

Because of this persistence and the resulting potential harm, several such compounds have been withdrawn from the market. Stocks of these compounds, in bulk, in small packages, and in formulations must be destroyed or converted to harmless or biodegradable forms or to chemicals useful in other ways.

If some or all of the chlorine atoms in these compounds can be removed, the toxicity is generally greatly reduced, the compounds can be more readily absorbed and degraded by the environment, and alternatively chemicals useful for other purposes can sometimes be produced.

After preliminary investigation of several alternative catalytic processes, hydrodechlorination was selected as a clean, relatively simple, widely applicable treatment. Because, unlike incineration, it does not drastically fragment the compounds treated, it has potential for production of useful products from large quantities of pesticides stored in bulk. In a properly designed process it does not produce a toxic off gas or contaminated aqueous residue. The process is adaptable to a trailer-mounted unit, thus meeting the objective of some EPA officials.

Studies at Worcester Polytechnic Institute were concentrated on catalytic hydrodechlorination of several compounds representative of types of the undesirable chlorinated species. These included:

1) Aroclor 1248 (representative of polychlorinated aromatics, in particular the polychlorinated biphenyls).
2) DDT, DDE, and DDD, the latter two may be thought of as partially dechlorinated DDT.
3) Dieldrin and Aldrin
4) Toxaphene (polychlorinated camphene)

Included in this report are extensive experimental data on the first two classes and data under selected conditions for the last two classes. These experimental results are interpreted both from the point of view of an understanding of the chemical reactions involved and the design of a reactor suitable for process use.

LITERATURE

In recent years several studies have been made of hydrodechlorination of chlorinated compounds according to the general reaction

$$R\text{-}Cl + H_2 \rightarrow R\text{-}H + HCl \qquad (1)$$

The reaction is usually carried out in the presence of an acidic acceptor such as NaOH.

The ease of reaction and the correspondent kinetics are strongly dependent on the structure of the carbon associated with the chlorine. The most common configurations encountered in our studies are polychlorinated organics containing a mixture of

1) mono and polychlorinated aliphatic
2) mono-and dichlorinated vinylic and allylic
3) aromatic

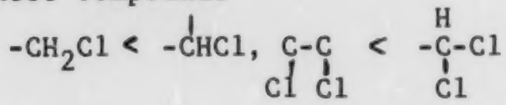
Previous studies have been concerned mainly with simpler molecules containing one of the above-mentioned carbon structures.

Noller and coworkers (1-7) have intensively studied the effect of ionic crystals ($CaSO_4$, $Ca(OH)_2$, CaO, etc.) and insulator (Al_2O_3) on mono and dichlorinated butene. Their investigations showed that the reactions start with an electron polarization followed by the rupture of C-Cl bond. According to this mechanism C-Cl bond rupture is facilitated by increasing the space char[illegible] on the cation, but the anion also has an effect.

Transition metals (Pt, Pd, Ni) have also been used by Berg et al. (8) to remove halogen from organic substances. These metals were prepared in different form (supported-Pd and Pt, Pt black and Raney nickel). The best results (highest rate) were achieved by Freifelder (9) using Pd on charcoal in the presence of an acid acceptor.

Raney nickel is also a good catalyst for hydrodechlorination although nickel itself is not highly resistant to the HCl coproduct (9). By using base as a HCl acceptor the effectiveness was improved but still it was necessary to use large amounts of catalyst (50-300%).

Horner et al. (10) have carried out hydrodechlorination reactions by using several types of halogen organics on Raney nickel. Their experiments resulted in a sequence of relative reactivities. According to this, primary aliphatic chlorine is the least reactive followed by the secondary and vicinal halogens. The geminal halogens proved to be highly reactive among these compounds



$$-CH_2Cl < -\overset{|}{C}HCl,\ \underset{Cl}{\overset{}{C}}-\underset{Cl}{C} < -\overset{H}{\underset{Cl}{C}}-Cl \qquad (2)$$

Kammerer et al. (11) also successfully used Raney nickel in the presence of alkali to hydrodechlorinate chlorobenzene.

A sequence of reactivity of a different group of compounds was established by Weiss and coworkers (12-15) by studying the reactions of vinyl chloride and cis and trans 1-2 dichloroethylenes on supported Pt catalyst. It was established on a mechanistic basis that the reactivity is increased in the sequence: aliphatic chlorine, vinyl chlorine and olefinic dichlorine.

Southwick (16) and Hasbrouck (17) have studied the hydrogenolysis of benzyl chloride and chlorobenzene respectively at room temperature and atmospheric pressure, on 5% Pd, Pt, and Rh on carbon catalysts. In both cases the activity sequence Pd > Pt > Rh was established. In the chlorobenzene (17) study, acetic acid, acetic acid + sodium acetate, ethanol, or ethanol + NaOH were used as solvents. These studies show that the choice of solvent affects the rate of reaction. The highest rates were attained using Pd on C plus ethanol and sodium hydroxide.

One general feature (16,17,18,19) observed is that activity decreases with conversion in batch reaction systems. Meschke and Hartung (18) have observed product inhibition (toluene) in the hydrogenolysis of benzyl alcohol. This behavior tends to obscure kinetic data in batch systems. Similar deviation from zero order behavior was observed in the hydrogenolysis of 4-dichloromethyl-4-methylcyclohexanol (20)

Berg, Diosady and Rees (8) have reported virtually quantitative hydrodechlorination of PCB at 180°C using 5% Pt or Pd catalyst on 60-80 mesh porous glass beads, as a technique for identifying PCB in a mixture of organic chlorine pesticides. No information was provided on the kinetics of the hydrodechlorination reaction. They report that at extreme severity, Aroclors can be hydrogenated and hydrodechlorinated completely to dicyclohexyl.

It is reported by Fleck and Haller (21) that 1,1-dichloro, (2-bisparachlorophenyl) ethane is easier to hydrodechlorinate than corresponding trichloro (2-bisparachlorophenyl) ethane. Most of these investigations were concerned with simple organic compounds that each contained only one type of C-Cl bond. This report addresses the question of whether or not chlorine atoms bonded to different groups in a single molecule retain the relative reactivity as determined from studies of simple molecules. It is also concerned with the relative hydrodechlorination activity of polychlorinated compounds.

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II EXPERIMENTAL REACTORS

Design of an appropriate catalytic hydrodechlorination process involves selection from a wide variety of operating conditions. Variables to be considered include:

1) Phase
    - Gas
    - Liquid-Gas: Two phase (sparged reactor, agitated reactor or trickle bed)

2) Catalyst
    - Active material
    - Support
    - Physical form (powder, granules, pellets, formed shapes)

3) Solvent

4) Acid acceptor (to combine with by-product HCl)

5) Batch or continuous operation

6) Severity variables
    a) Temperature
    b) Pressure
    c) Catalyst quantity
    d) Time

7) Catalyst selectivity

Data representative of this range of variables cannot be obtained in one piece of equipment. For these studies several reactors were used, each of particular value for selected sets of variables. In future studies of different compounds these same reactors would be appropriate. They are described in sufficient detail to permit purchase or construction of similar equipment.

PULSED MICROREACTOR

The principal utility of the pulsed microreactor is for screening purposes - for rapid selection of useful catalyst types, for rough choice of pressure, temperature and reaction time needed for a particular reaction. As set up at WPI the pulse microreactor is particularly useful for analysis of reaction products since it is a part of a gas chromatograph assembly and can be coupled to a mass spectrometer for product identification. By definition a pulsed microreactor is a system where a pulse of reactant is adsorbed, reacted, and desorbed on a catalyst bed in a short period of time. Our reactor is the glass liner of the injection port of a Perkin Elmer 900 gas chromatograph, Fig. (2-1) The injector port consists of an aluminum block which can be heated from ambient to 400°C. The precision ground glass liner slides into the heated block and is retained by a spring, metal insert, and septum cap. Carrier gas is introduced into the heated block and passes through an annulus and into the 1 mm channel in the glass liner. Temperature traverses along the length of the liner with He carrier gas flowing showed there was a zone 2 cm long where the temperature varied less than ±1°C.

Catalyst beds typically 2 to 10 mm long containing 2 to 10 mg of 40-60 mesh ground catalysts were placed in the isothermal zone and sandwiched between plugs of pyrex wool. Catalysts are then pretreated at elevated temperature in flowing carrier gas, e.g., the supported metal catalysts were reduced at 250°C with 30 cc/min STP H_2 for two hours and the reduction was monitored chromatographically. After the catalyst is pretreated, 0.5-2.0μl samples of organochlorine compound in solvent are injected into the inlet, reacted and passed directly to a 5 ft OV-1 column for separation and analysis. Although the residence times calculated on the basis of carrier gas flow rate are on the order of 10^{-2} sec, reactants have been observed to remain adsorbed on the bed for several minutes depending on temperature, catalyst surface area, and volatility of the reacting mixture. Thus the concept of rate must be carefully evaluated within these constraints.

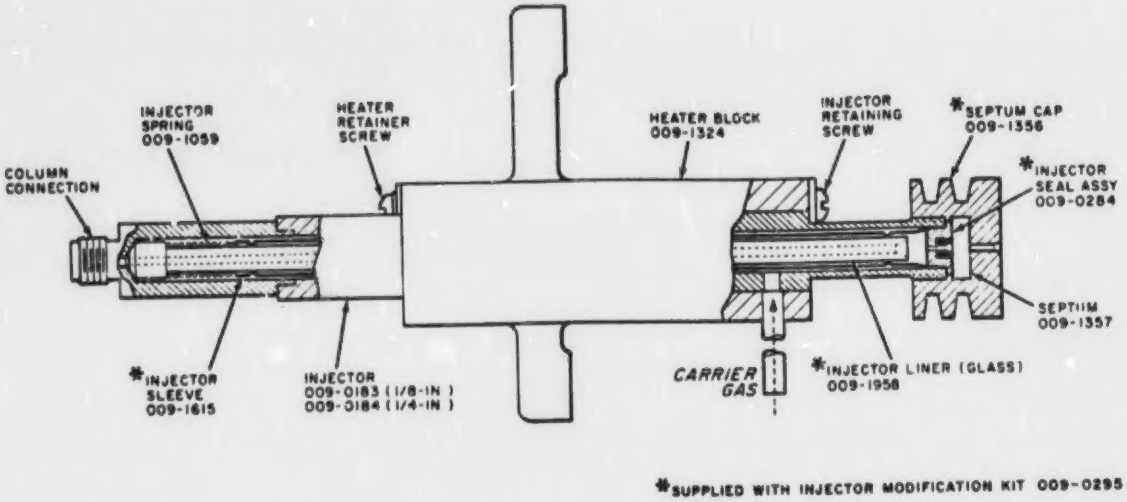
CONTINUOUS VAPOR PHASE REACTOR

The continuous flow process alternative is to vaporize the chlorinated organic compound into a stream of heated carrier gas. The mixed gas is then passed through a heated tubular reactor containing catalyst. The use of a continuous reactor is especially suited for catalyst deactivation studies.

The continuous gas phase reactor used in these studies Fig. (2-2) consisted of a gas-feed, control and purification system, liquid introduction system, vaporizer,

Figure (2-1)

PULSED MICROREACTOR


INJECTOR SPRING 009-1059
HEATER RETAINER SCREW
HEATER BLOCK 009-1324
INJECTOR RETAINING SCREW
*SEPTUM CAP 009-1356
COLUMN CONNECTION
*INJECTOR SEAL ASSY 009-0284
SEPTUM 009-1357
*INJECTOR SLEEVE 009-1615
INJECTOR 009-0183 (1/8-IN) 009-0184 (1/4-IN)
CARRIER GAS
*INJECTOR LINER (GLASS) 009-1958
*SUPPLIED WITH INJECTOR MODIFICATION KIT 009-0295

- Model 900 Liquid Sample Injection System (Top View)

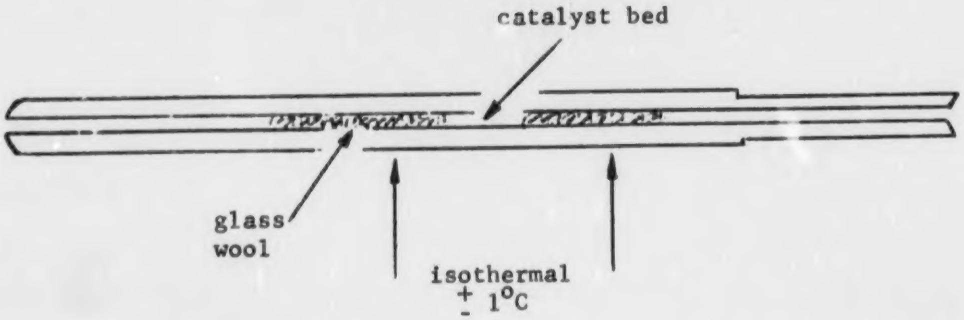
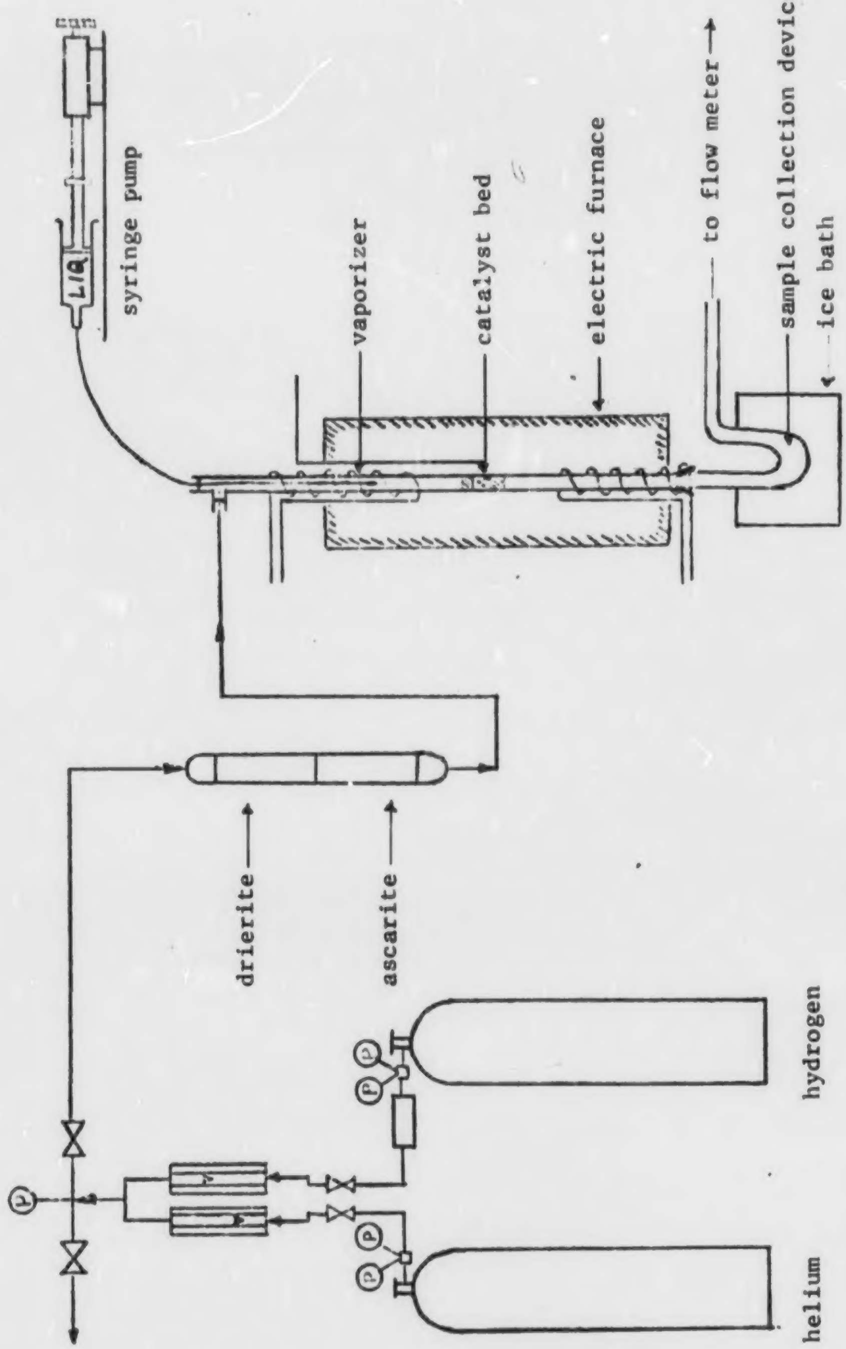


Figure (2-2)

CONTINUOUS VAPOR PHASE REACTOR



tubular reactor, and sample collection device. Hydrogen and Helium are obtained from AIRCO and A.I.M. respectively with purity of greater than 99.9%. Gas flows are controlled by 2 stage regulators, needle valves and rotameters. Trace O_2 is removed from hydrogen by means of a Deoxo catalyst and trace H_2O and CO_2 are removed from both streams by a packed bed of drierite and ascarite respectively.

Solutions of pesticides typically 1-5% by weight in P-Xylene (spectro grade Aldrich Chemical Co.) are metered by a Harvard Apparatus compact infusion pump equipped with a 50cc Hamilton gas tight syringe. The gas and liquid feed are preheated and the liquid vaporized off the end of a teflon capillary prior to the catalyst bed.

The reactor is fabricated from 6 mm I.D. pyrex tubing mounted vertically (gas flow directed downward) and the exit end consists of a heated female ground glass joint to accept the product receiver.

Both the vaporizer (entrance end) and ground glass joint (exit end) are wrapped with heating tape for individual temperature control sufficient to vaporize the feed and keep products from condensing. This whole assembly is mounted in a tubular electric furnace which controls the catalyst bed temperature.

Catalyst beds typically 1-3 mm long containing 20-30 mg of 60-80 mesh ground catalyst are sandwiched between plugs of glass wool and located at the isothermal center of the tubular electric furnace.

The receiver consists of a U tube immersed in a cold trap. A male ground glass joint connects the receiver with the exit end of the reactor. This joint then is heated by the exit end of the tubular reactor and ensures that initial condensation of the product occurs only within the collection device, not on the reactor exit walls. Total gas flow rates are measured by a bubble flow meter connected to the outlet of the cold trap.

LIQUID PHASE REACTORS

The batch process alternative is to conduct hydrodechlorination reactions in the liquid phase. Pesticide solutions are slurried with a supported metal catalyst in a well stirred reaction vessel. It is desirable to use an autoclave to be able to operate at elevated temperature to increase reaction rates and elevated pressure to increase the concentration of the reactant gas (Hydrogen) in the liquid phase. Several liquid phase reactors were used in these studies.

1) LOW PRESSURE GLASS REACTOR

An apparatus was designed to measure hydrogen uptake and product distribution simultaneously, as shown in Figs. (2-3,4). The reaction vessel (1) is surrounded by a water jacket connected to a thermostat. A burette (2) filled with mercury can measure the hydrogen uptake at constant pressure (atmospheric) and the differential manometer (3) filled with light liquid acts as a null-indicator. By using the syringe (4) a small amount of sample can be taken from the reactor for chromatographic analysis.

Operating procedure for this reactor was as follows:

(1) 50% of the solvent and all of the catalyst were placed in the reactor and maintained under a hydrogen atmosphere.

(2) at zero time a solution containing the remaining 50% of the solvent, the reactant, and sodium hydroxide was introduced into the reactor.

(3) samples were withdrawn at appropriate time intervals.

2) HIGH PRESSURE STIRRED REACTORS

a. Teflon Lined Autoclave

A modified 750 cc stainless steel teflon lined autoclave Figs. (2-5,6) manufactured by Berghof GmbH was used for liquid phase studies at elevated hydrogen pressure. The reactor is provided with a Teflon liner which makes it possible to handle reactions in which a highly corrosive product (e.g. HCl) is formed. Teflon

Figure (2-3)

LOW PRESSURE GLASS REACTOR

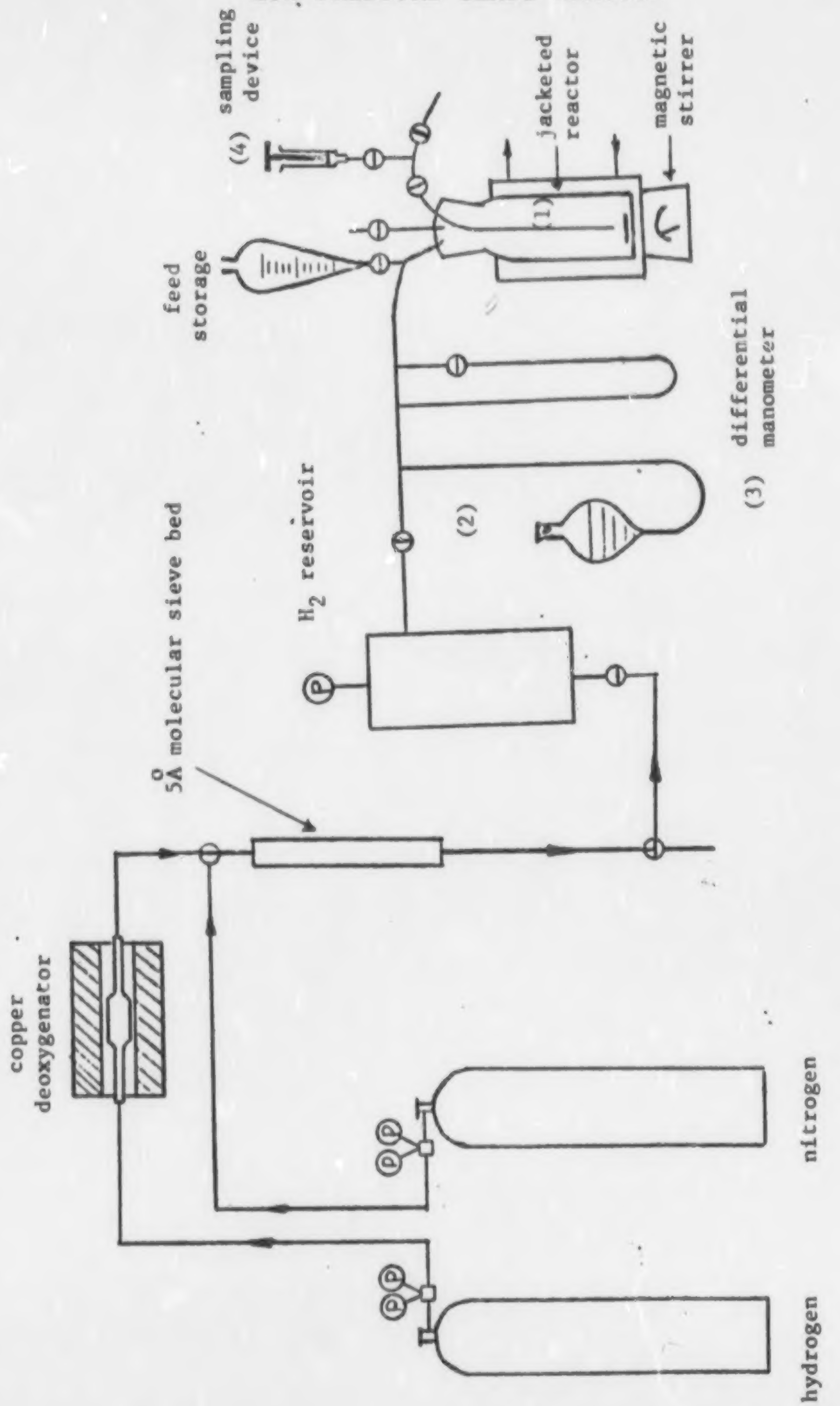


Figure (2-4)

LOW PRESSURE GLASS REACTOR

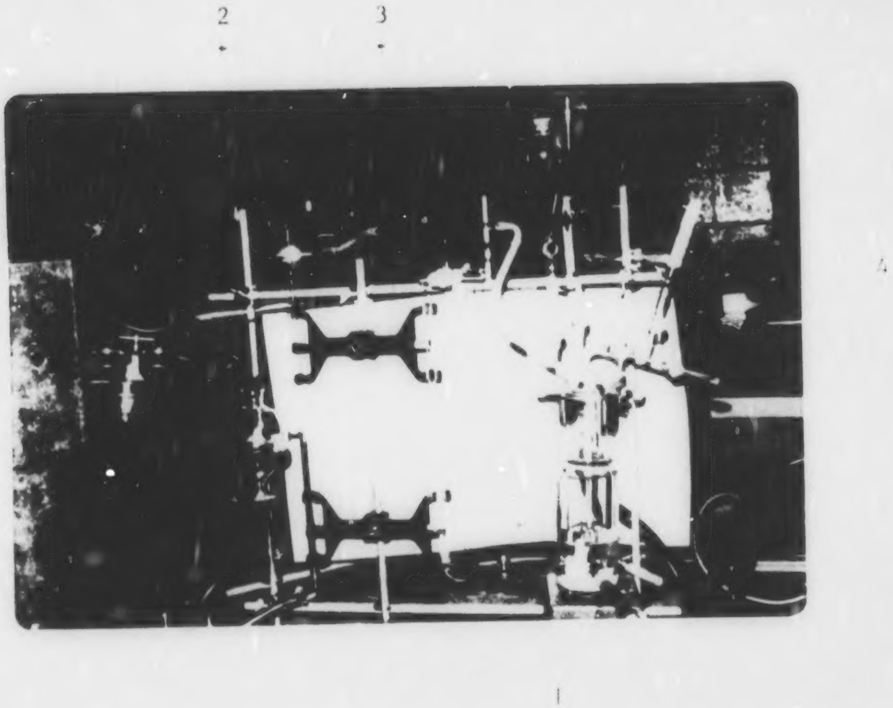


Figure (2-5)

HIGH PRESSURE TEFLON LINED AUTOCLAVE

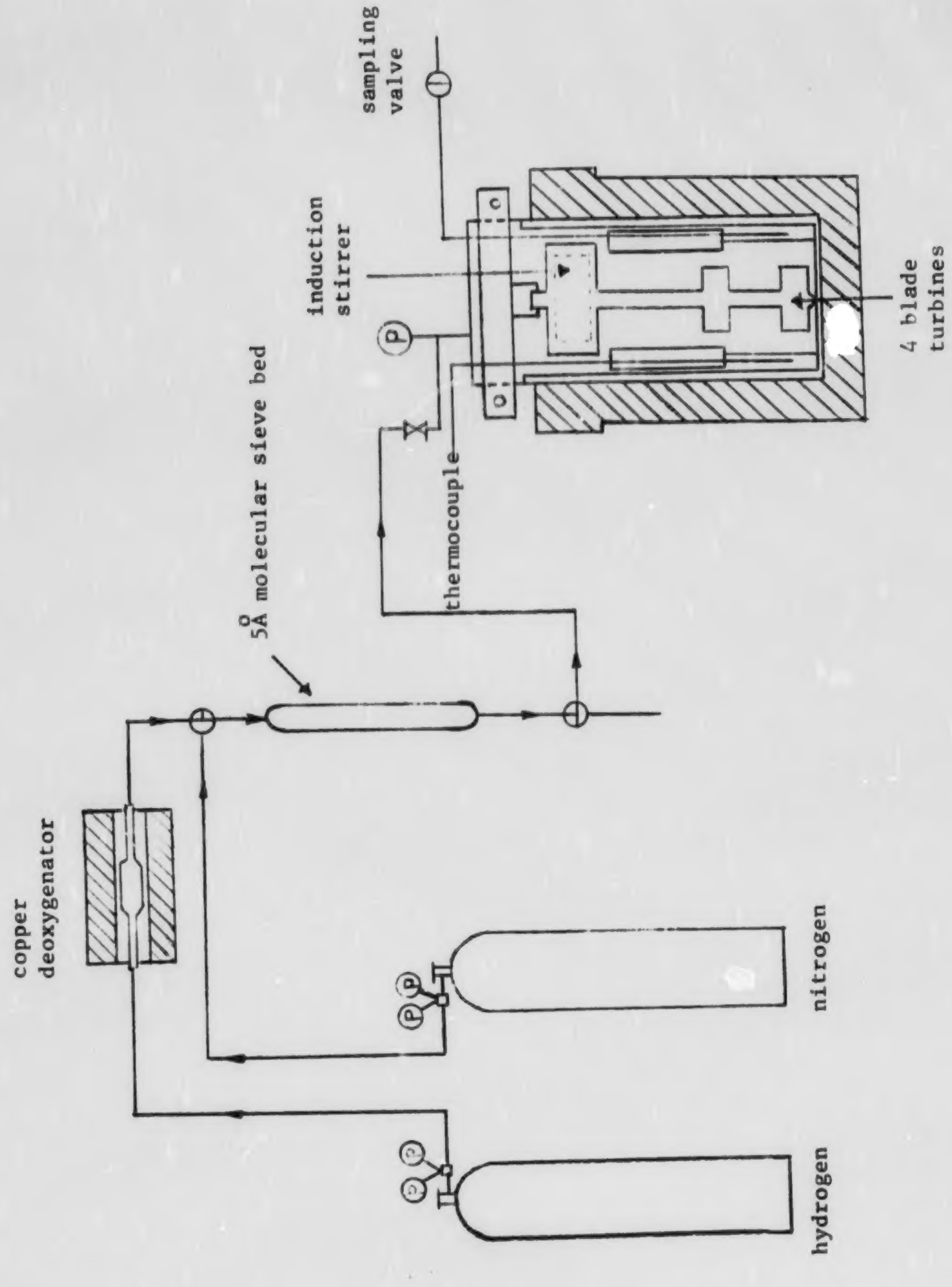


Table (3a-1)

PULSE MICROREACTOR AROCLOR 1248 HYDRODECHLORINATION

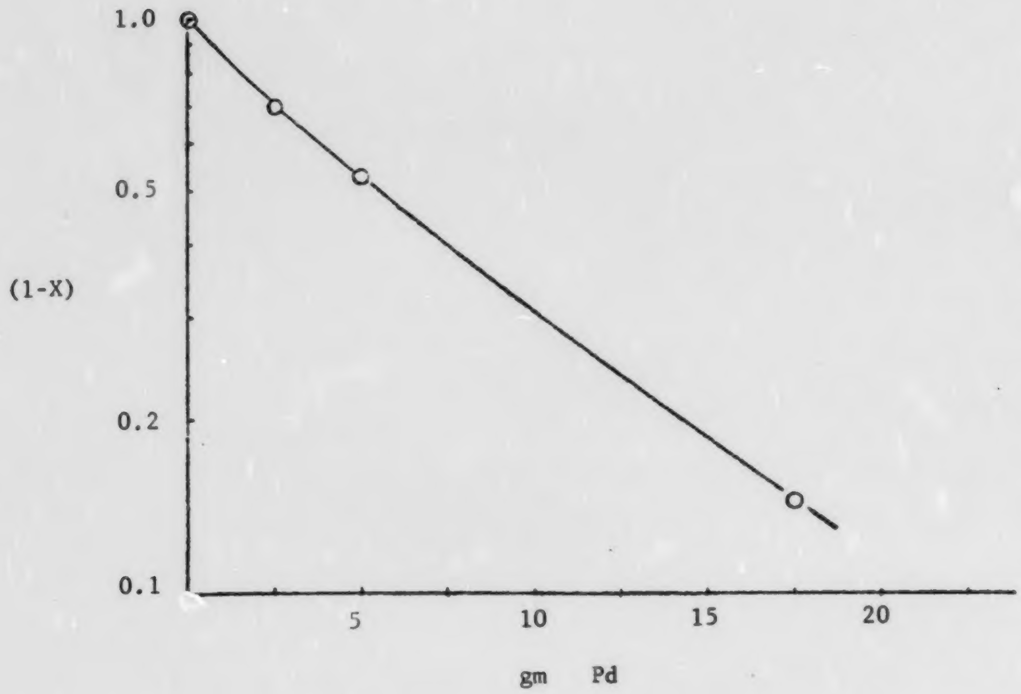
220°C 2.3 ATM H_2 $\tau \approx .01$ sec.

Catalyst wt (mg)	5.0	4.6	5.0	5.0
wt % Pd	.00	.05	.10	.35
$\phi\phi_o$	—	.134	.296	.758
$\phi\phi_1$	.003	.058	.068	.043
$\phi\phi_2$	.013	.129	.140	.094
$\phi\phi_3$	.305	.337	.279	.078
$\phi\phi_4$	.493	.236	.166	.026
$\phi\phi_5$	.189	.091	.046	—
X	.013	.304	.469	.855

Figure (3a-1)

PULSE MICROREACTOR AROCLOR 1248 HYDRODECHLORINATION

220°C 2.3 ATM H_2 .01 sec.



held at pressure and temperature for a specified period of time, cooled as rapidly as possible and then the products were analyzed. In later experiments continuous sampling was utilized. Tables (3a-2,3) respectively list experimental conditions and product analyses for preliminary experiments using Girdler G49-A 61.0% Ni on Kieselguhr catalyst, ethanol as a solvent and sodium hydroxide as an acid acceptor. Several important results were derived from this set of experiments.

1) Complete hydrodechlorenation of PCB can be obtained using an inexpensive Ni catalyst at elevated temperature and pressure in a reasonable 6 hour time period (Experiment 16).
2) The reaction rate still has a positive dependence on hydrogen pressure above 25 atmospheres (Experiment 15 vs Experiment 17).
3) Catalyst poisoning occured at 175°C (Experiment 21) which places an upper limit on reaction temperature.

The following experimental data is derived from four experiments where 100 gms of 2 wt% Aroclor 1248 in ethanol were reacted at 50 atm. H_2 pressure with 200 mg Girdler G49-A and with 110% of the NaOH required to neutralize all HCl produced by complete hydrodechlorination. The four experiments EPA 7, 10, 6, 8, were conducted at 60, 80, 100, and 130°C respectively. Selectivity data obtained at these four temperatures were sufficiently similar so that they could be treated as one set of experimental data. Analytical data for this set of experiments are given in table (3a-4) where several samples were taken during each experiment. Figs. (3a-2,3, and 4) are plots of the relative product distribution data

$$\frac{\phi\phi_i}{\sum_{i=o}^{5} \phi\phi_i}$$

Table (3a-2)

PRELIMINARY LIQUID PHASE AROCLOR EXPERIMENTAL CONDITIONS

Run#	1	3	5	15	16	17	18	19	20	21
Aroclor 1248 (gm)	5.27	4.57	11.0	13.3	12.19	11.29	12.01	12.96	10.67	11.45
Aroclor 1248 (gm mole)	.0180	.0157	.0377	.0455	.0417	.0387	.0411	.0444	.0365	.0392
Ethanol (gm.)	98.6	86.8	110.5	131.8	110	102	108	117	96	103
Wt. % Aroclor 1248	5.07	5.00	9.05	7.38	9.98	9.97	10.01	9.97	10.00	10.00
NaOH gms	4.0	2.6	6.4	7.3	6.66	6.12	6.50	7.04	5,80	6.23
NaOH (gm-mole)	0.100	.065	.160	.183	.167	.153	.164	.176	.145	.156
$\frac{\text{NaOH}}{\text{Aroclor 1248}}$	5.5	4.1	4.2	4.0	4.0	3.95	3.99	3.96	3.97	3.97
Ni on Kieselguhr	2.5	0.55	1.1	1.39	1.25	1.12	1.23	1.30	1.08	1.11
↘ $\frac{\text{wt. Aroclor}}{\text{wt. catalyst}}$	2.1	8.3	10.0	9.6	9.75	10.08	9,76	9,97	9.88	10.32
Reaction time (hrs)	2	2	4	2	6	2	2	4	1.2	2
Pressure (Bar)	50	50	50	50	50 (50-42)	25 (25-21)	50 (50-48)	50 (54-47)	0(atm)	50 (50-60)
Temperature ^{o}C	100	100	100	100	100-115	100-110	25	100	25-100	175
Chlorine Conversion X	.628	.293	.574	.559	1.000	.390	.099	.888	0.00	.107

Table (3a-3)

PRODUCT COMPOSITION (FOR PRELIMINARY LIQUID PHASE AROCLOR EXPERIMENTS)

Product Analysis, mole %

Run #	Reactant Mole %	1	3	5	15	16	17	18	19	20	21
$\phi\phi_o$	0	45.2	19.9	32.3	32.59	99.99	6.45	0	72.42	0	2.96
$\phi\phi_1$	0.06	10.2	1.0	13.8	13.20	0	12.45	0	12.53	0.13	0.58
$\phi\phi_2$	0.53	15.7	6.9	17.4	19.61	0	30.94	0.50	13.94	0.50	4.59
$\phi\phi_3$	24.09	16.5	30.5	20.7	22.08	0.004	34.00	24.32	1.12	23.41	36.96
$\phi\phi_4$	57.59	11.5	37.0	11.9	11.64	0	15.79	60.19	0	57.69	50.96
$\phi\phi_5$	17.74	0.9	4.9	1.8	1.51	0	0	15.00	0	18.24	5.07
Atoms Cl/biphenyl	3.92	1.46	2.77	1.67	1.73	0.00	2.39	3.53	0.44	3.93	3.5
Cl Conversion X %		62.8	29.3	57.4	55.9	100.0	39.0	9.9	88.8	0.00	10.7

Table (3a-4)

ANALYTICAL DATA LIQUID PHASE Ni CATALYZED AROCLOR 1248 HYDRODECHLORINATION

Sample #			Aroclor	10-1	6-2	10-2	7-8	8-1	8-2	8-3	6-3
Cl Conv. X			1248	.003	.010	.026	.031	.051	.084	.176	.194
O-Cl	M&P-Cl	RT*	Product Analysis, mole fraction								
0	0	5.0									
0	0	6.8			.0039		.0083	.0030	.0044	.0154	.0435
1	0	9.8	.0009				.0043	.0056	.0037	.0128	.0119
0	1	11.2			.0018		.0012	.0033	.0061	.0211	.0275
0	1	11.3									
2	0	12.4	.0015	.0016	.0032	.0045	.0046	.0059	.0072	.0214	.0166
1	1	13.0		.0032	.0008	.0033	.0010	.0038	.0075	.0163	.0208
1	1	13.5	.0052	.0056	.0086	.0134	.0112	.0206	.0358	.0077	.0075
1	1	13.8								.0641	.0548
1	1	13.9									
1	1	14.8							.0015		
3	0	15.1	.0025	.0016	.0032	.0033	.0026	.0039	.0032	.0062	.0069
2	1										SFS**
2	1	15.7	.0658	.0701	.0740	.0851	.0785	.0890	.1081	.1534	.1583
2	1	16.2	.0021					.0029		.0041	
2	1	16.5	.0099	.0087	.0097	.0117	.0103	.0120	.0128	.0641	.0646
2	1	16.7	.0144		.0154	.0209	.0181	.0247	.0310		
1	2	17.0	.0054	.0141	.0041	.0061	.0051	.0080	.0093	.0134	.0120
1	2	17.4	.0993	.0964	.0940	.0916	.0960	.0912	.0891	.0708	.0657
1	2	17.9	.0422	.0431	.0439	.0630	.0511	.0687	.0831	.1076	.0911
1	2	SBS*** →									
1	2	18.4	.0177	.0135	.0153	.0170	.0156	.0194	.0207	.0213	.0182
2	2	18.8	.1768	.1853	.1806	.1763	.1817	.1763	.1756	.1477	.1476
2	2	19.1					SBS →				
2	2	20.0	.0926	.0909	.0925	.0890	.0924	.0885	.0891	.0729	.0658
2	2					SFS →					
2	2	20.4	.0625	.0684	.0651	.0681	.0667	.0635	.0629	.0494	.0459
1	3	20.9	.0470	.0423	.0433	.0378	.0399	.0344	.0301	.0177	.0185
1	3	21.3	.1446	.1521	.1459	.1341	.1451	.1240	.1113	.0648	.0431
1	3			SBS →							.0187
3	2	21.8	.0086	.0093	.0091	.0072	.0075	.0072	.0052		
3	2		SFS →							.0083	.0095
3	2	22.3	.0785	.0788	.0771	.0696	.0743	.0659	.0569	.0234	.0173
2	3	22.6	.0130	.0162	.0182	.0166	.0130	.0128	.0126	.0078	.0129
2	3	23.1	.0131	.0402	.0114	.0229	.0085	.0134	.0062	.0025	.0031
2	3	23.4	.0209	SBS	.0196	.0154	.0162	.0138	.0089	.0034	.0037
2	3										
2	3	23.7	.0283	.0238	.0246	.0199	.0205	.0176	.0090	.0006	.0009
1	4	24.4	.0274	.0205	.0226	.0178	.0170	.0152	.0083	.0017	
1	4	25.0	.0035		.0020		.0006				
1	4	25.7	.0131	.0074	.0083	.0039	.0090	.0050			

* OV 17 Retention Time (min)

** Shoulder on Leading Edge of Following Peak

*** Shoulder on Tailing Edge of Preceding Peak

Table (3a-4)

ANALYTICAL DATA LIQUID PHASE Ni CATALYZED AROCLOR 1248 HYDRODECHLORINATION

Sample #			7-9	8-5	8-7	8-9	7-10	8-11	10-3	8-12	6-4
Cl Conv. X			.239	.276	.375	.461	.428	.469	.488	.490	.554
O-Cl	M&P-Cl	RT*	Product Analysis, mole fraction								
0	0	5.0	.0012				.0034	.0006	.0009	.0008	.0014
0	0	6.8	.0450	.0345	.0697	.0908	.1213	.1249	.0730	.1427	.2747
1	0	9.8	.0180	.0275	.0486	.0587	.0550	.0714	.0420	.0778	.0519
0	1	11.2	.0261	.0467	.0636	.0204	.0208	.0249	.0730	.0278	.0262
0	1	11.3				.0731	.0565	.0852		.0897	.0649
2	0	12.4	.0330	.0426	.0721	.0842	.0887	.0990	.0499	.1059	.0578
1	1	13.0	.0150	.0239	.0277	.0283	.0231	.0276	.0354	.0270	.0404
1	1	13.5	.0153	.0171	.0243	.0278	.0324	.0282	.0132	.0286	.0155
1	1	13.8	.0700	.0908	.1062	.0618	.0974	.1013	.0669	.0977	.0736
1	1	13.9									
1	1	14.8				.0007		.0011		.0012	
3	0	15.1	.0093	.0107	.0102	.0133	.0154	.0143	.0110	.0136	.0131
2	1		SFS**	→	→	→	→	→	→	→	→
2	1	15.7	.1546	.1874	.2083	.2025	.1735	.1906	.1453	.1831	.1564
2	1	16.2	.0054	.0051			.0054		.0040		.0052
2	1	16.5	.0789	.0737	SFS	→	→	→	→	→	→
2	1	16.7			.0755	.0716	.0795	.0663	.0567	.0630	.0618
1	2	17.0	.0158	.0133	.0099	.0082	.0089	.0056	.0071	.0046	.0063
1	2	17.4	.0611	.0465	.0263	.0186	.0200	.0107	.0267	.0100	.0138
1	2	17.9	.1092	.1086	.0920	.0796	.0780				
1	2		SBS***	→	→	→	→	.0746	.0503	.0582	.0473
1	2	18.4	.0193	.0181	.0103	.0069	.0052		.0059		
2	2	18.8	.1320	.1147	.0802	.0482	.0501	.0335	.0785	.0297	.0442
2	2	19.1	SBS	→	→	.0181	.0157	.0170	SBS	.0136	.0146
2	2	20.0	.0604	.0537	.0299	.0227	.0222	.0190	.0271	.0187	.0150
2	2	20.4	.0434	.0327	.0172	.0106	.0166	SBS	.0184	SBS	.0049
2	2		SBS	→	→	→					
1	3	20.9	.0134	.0103	.0035	.0018	.0021		.0060		
1	3	21.3	.0361	.0183	SFS	.0022	.0028	.0010	.0215	.0017	.0021
1	3		.0130	.0119	.0062		.0032				
3	2	21.8									
3	2		.0065	.0034					.0020		
3	2	22.3	.0121	.0079	.0018	.0013	.0007		.0047		
2	3	22.6									
2	3	23.1	.0016								
2	3	23.4	.0030	.0008							
2	3										
2	3	23.7									
1	4	24.4									
1	4	25.0									
1	4	25.7									

* OV 17 Retention Time (min)
** Shoulder on Leading Edge of Following Peak
*** Shoulder on Tailing Edge of Preceding Peak

Table (3a-4)

ANALYTICAL DATA LIQUID PHASE Ni CATALYZED AROCLOR 1248 HYDRODECHLORINATION

Sample #			6-5	10-4	6-6	10-3	10-6	6-7	6-8	10-7	6-9
Cl Conv. X			.686	.732	.750	.796	.824	.837	.875	.957	.959
O-Cl	M&P-Cl	RT*	Product Analysis, mole fraction								
0	0	5.0	.0037	.0033	.0049	.0046	.0060	.0064	.0069	.0140	.0099
0	0	6.8	.4297	.5120	.5101	.6047	.6515	.6489	.7069	.8978	.8869
1	0	9.8	.0730	.0669	.0813	.0697	.0686	.0879	.0862	.0370	.0507
0	1	11.2	.0288	.0746	.0278	.0612	.0517	.0184	.0154	.0049	.0069
0	1	11.3	.0642		.0582			.0413	.0333		
2	0	12.4	.0743	.0680	.0788	.0660	.0646	.0793	.0753	.0255	.0371
1	1	13.0	.0342	.0308	.0276	.0247	.0215	.0148	.0094		
1	1	13.5	.0123	.0099	.0099	.0067	.0053	.0049	.0032	.0014	
1	1	13.8	.0554	.0498	.0438	.0356	.0295	.0198	.0129	.0016	.0005
1	1	13.9									
1	1	14.8									
3	0	15.1	.0141	.0121	.0138	.0122	.0115	.0130	.0116	.0050	.0047
2	1										
2	1	15.7	.1092	.0903	.0807	.0661	.0517	.0401	.0256	.0037	.0022
2	1	16.2									
2	1	16.5									
2	1	16.7	.0406	.0317	.0271	.0230	.0138	.0091	.0058		
1	2	17.0									
1	2	17.4	.0022	.0009	.0008						
1	2	17.9	.0232	.0187	.0178	.0129	.0103	.0079	.0056	.0021	
1	2										
1	2	18.4									
2	2	18.8	.0177	.0127	.0103	.0056	.0074	.0018	.0022	.0005	
2	2	19.1	.0086	.0080	.0045			.0010			
2	2	20.0	.0049	.0032	.0021						
2	2										
2	2	20.4	SBS***								
1	3	20.9									
1	3	21.3									
1	3										
3	2	21.8									
3	2										
3	2	22.3									
2	3	22.6									
2	3	23.1									
2	3	23.4									
2	3										
2	3	23.7									
1	4	24.4									
1	4	25.0									
1	4	25.7									

* OV 17 Retention Time (min)
** Shoulder on Leading Edge of Following Peak
*** Shoulder on Tailing Edge of Preceding Peak

Figure (3a-2)

AROCLOR 1248 RELATIVE PRODUCT DISTRIBUTION DATA

50 ATM H_2 , Ni on Kieselguhr

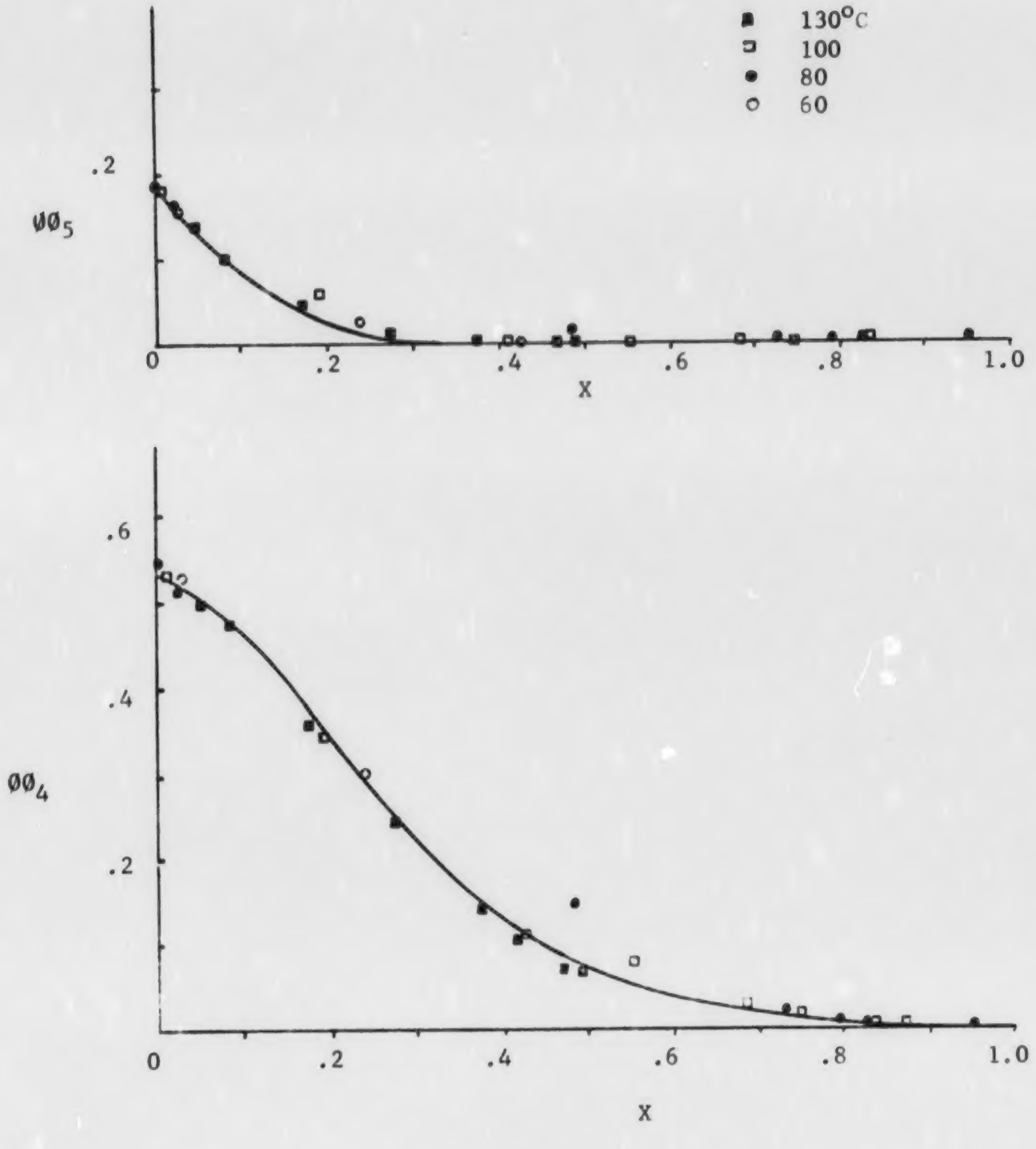
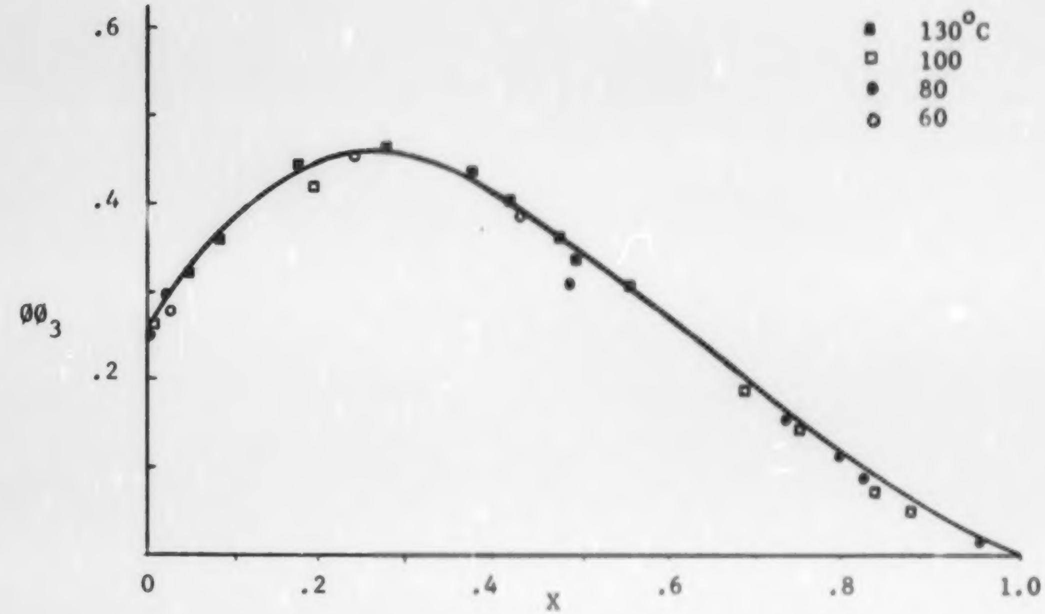


Figure (3a-3)

AROCLOR 1248 RELATIVE PRODUCT DISTRIBUTION DATA

50 ATM H_2 , Ni on Kieselguhr



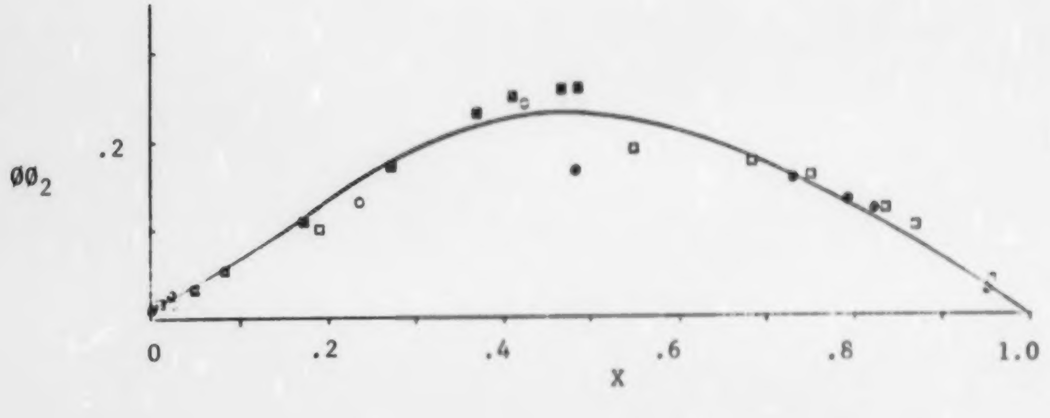
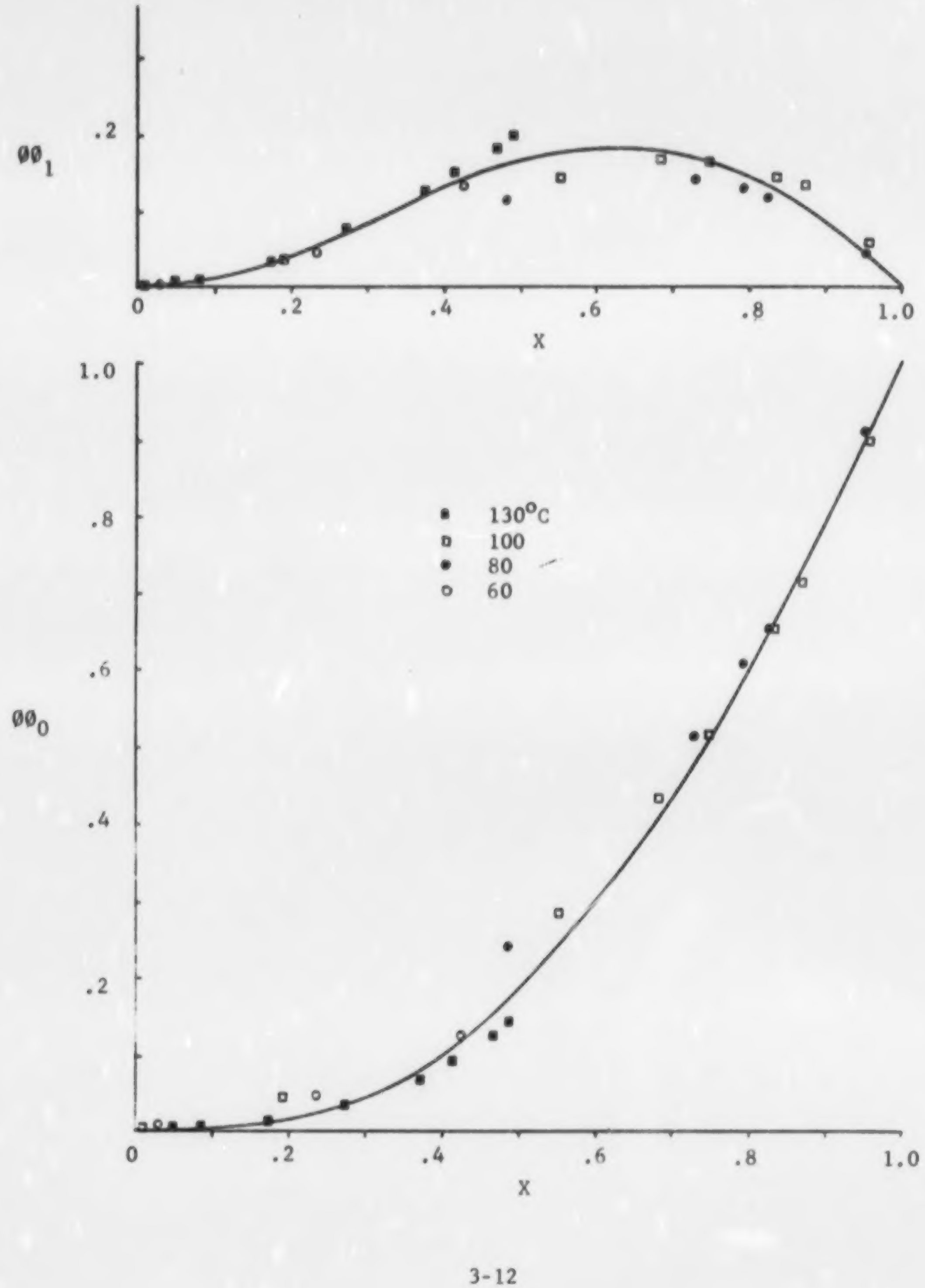


Figure (3a-4)

AROCLOR 1248 RELATIVE PRODUCT DISTRIBUTION DATA

50 ATM H_2 , Ni on Kieselguhr



vs chlorine conversion X

These observed selectivity data were filled to a consecutive reaction scheme

$$\phi\phi_5 \xrightarrow{k_{54}} \phi\phi_4 \xrightarrow{k_{43}} \phi\phi_3 \xrightarrow{k_{32}} \phi\phi_2 \xrightarrow{k_{21}} \phi\phi_1 \xrightarrow{k_{10}} \phi\phi_0$$

described by a set of first order reaction path expressions.

$$\frac{d\phi\phi_4}{d\phi\phi_5} = \frac{k_{43}}{k_{54}} \frac{\phi\phi_4}{\phi\phi_5} - 1$$

$$\frac{d\phi\phi_3}{d\phi\phi_5} = - \frac{k_{43}\phi\phi_4 - k_{32}\phi\phi_3}{k_{54}\phi\phi_5}$$

$$\frac{d\phi\phi_2}{d\phi\phi_5} = - \frac{k_{32}\phi\phi_3 - k_{21}\phi\phi_2}{k_{54}\phi\phi_5}$$

$$\frac{d\phi\phi_1}{d\phi\phi_5} = - \frac{k_{21}\phi\phi_2 - k_{10}\phi\phi_1}{k_{54}\phi\phi_5}$$

$$\frac{d\phi\phi_0}{d\phi\phi_5} = - \frac{k_{10}\phi\phi_1}{k_{54}\phi\phi_5}$$

The best fit was obtained with the following set of relative rate constants.

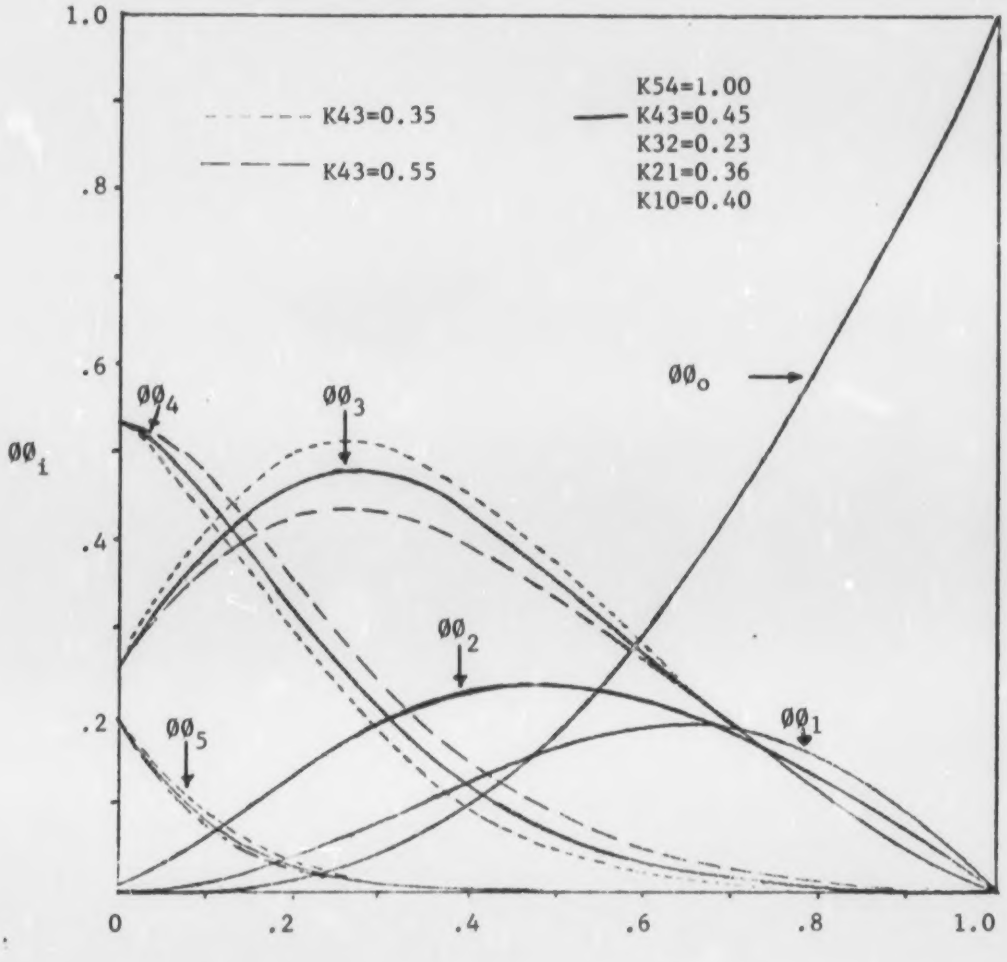
$\frac{k_{43}}{k_{54}}$	$\frac{k_{32}}{k_{54}}$	$\frac{k_{21}}{k_{54}}$	$\frac{k_{10}}{k_{54}}$
0.40	0.23	0.36	0.40

The curves obtained using this set of constants are superimposed on the data in figs. (3a-2,3 and 4). Figure (3a-5) shows the effect of varying the value of a relative rate constant $\frac{k_{43}}{k_{54}}$ from 0.35 to 0.55 on the computed reaction paths. The fit for $\frac{k_{43}}{k_{54}} = 0.40$ is sufficiently unique that it is reasonable to conclude that the absolute error in any of the relative rate constants is less than 0.05.

Using assumed absolute first order kinetics and the calculated values of the relative rate constants, a semilog plot of (1-X) vs time (fig. 3a-6) is slightly convex in shape due to the fact that the relative rate constants pass through a minimum at $\frac{k_{32}}{k_{54}} = 0.23$, according to the computed solution. The experimentally

Figure (3a-5)

SENSITIVITY OF INTERMEDIATE SELECTIVITIES TO RELATIVE RATE CONSTANT k_{43}



X

observed behavior (fig. 3A-7) was quite different.(1)The reaction exhibits an induction period which we have found to be characteristic of in situ additional reduction of the prereduced and stabilized G 49-A catalyst (see section III B) and (2) after this induction period the curve is concave in nature.

This behavior can be rationalized by considering Langmuir Hinshelwood kinetics, which also qualitatively explains why the values of relative rate constants passes through a minimum with number of chlorine atoms per molecule.

Consider that each of the relative rate constants determined is really the product of a kinetic term $k^*_{i,i-1}$ and an adsorption equilibrium constant K_i. Each absolute rate expression however is most likely of the form

$$\frac{d\phi\phi_i}{dt} = \frac{(k^*_{i+1,i}\,K_{i+1}\,\phi\phi_{i+1} - k^*_{i,i-1}\,K_i\,\phi\phi_i)\,P_{H_2}^n}{(1+\sum_{i=0}^{5} K_i\,\phi\phi_i + K_{solvent}\,C^s_{solvent} + (K_{H_2}P_{H_2})^n)^m}$$

where total chlorine conversion with time is represented by

$$\frac{dX}{dt} = \frac{-\sum_{i=0}^{5} i\,\frac{d\phi\phi_i}{dt}}{\sum_{i=0}^{5} i\,\phi\phi_i^o}$$

Detailed studies to determine every $k^*_{i,i-1}$ and K_i value and thus quantitatively describe the absolute kinetics have not been attempted. Note however that the

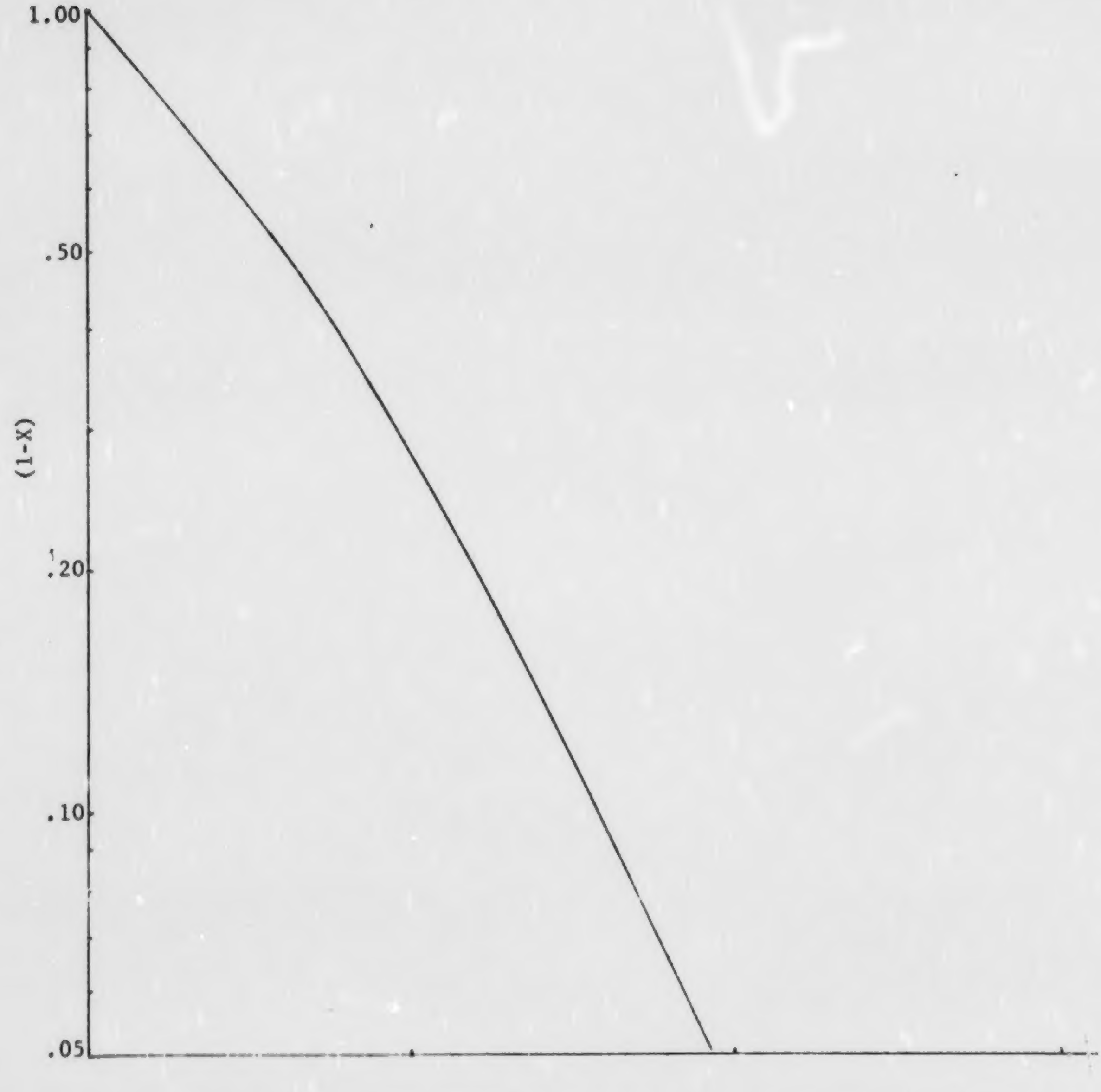
$$\frac{P_{H_2}^n}{(1+\sum_{i=0}^{5} K_i\,\phi\phi_i + K_{solvent}\,C^s_{solvent} + (K_{H_2}P_{H_2})^n)^m}$$

term is common to each rate expression so that the reaction paths degenerate to simple first order power law kinetics when absolute rate expressions are divided as we have shown. The fact that the relative rate constants pass through a minimum suggests that product inhibition effects will be observed in batch hydrodechlorination of PCB especially as the concentration of starting material is increased.

In the course of these studies it was observed that within each group of PCB

Figure (3a-6)

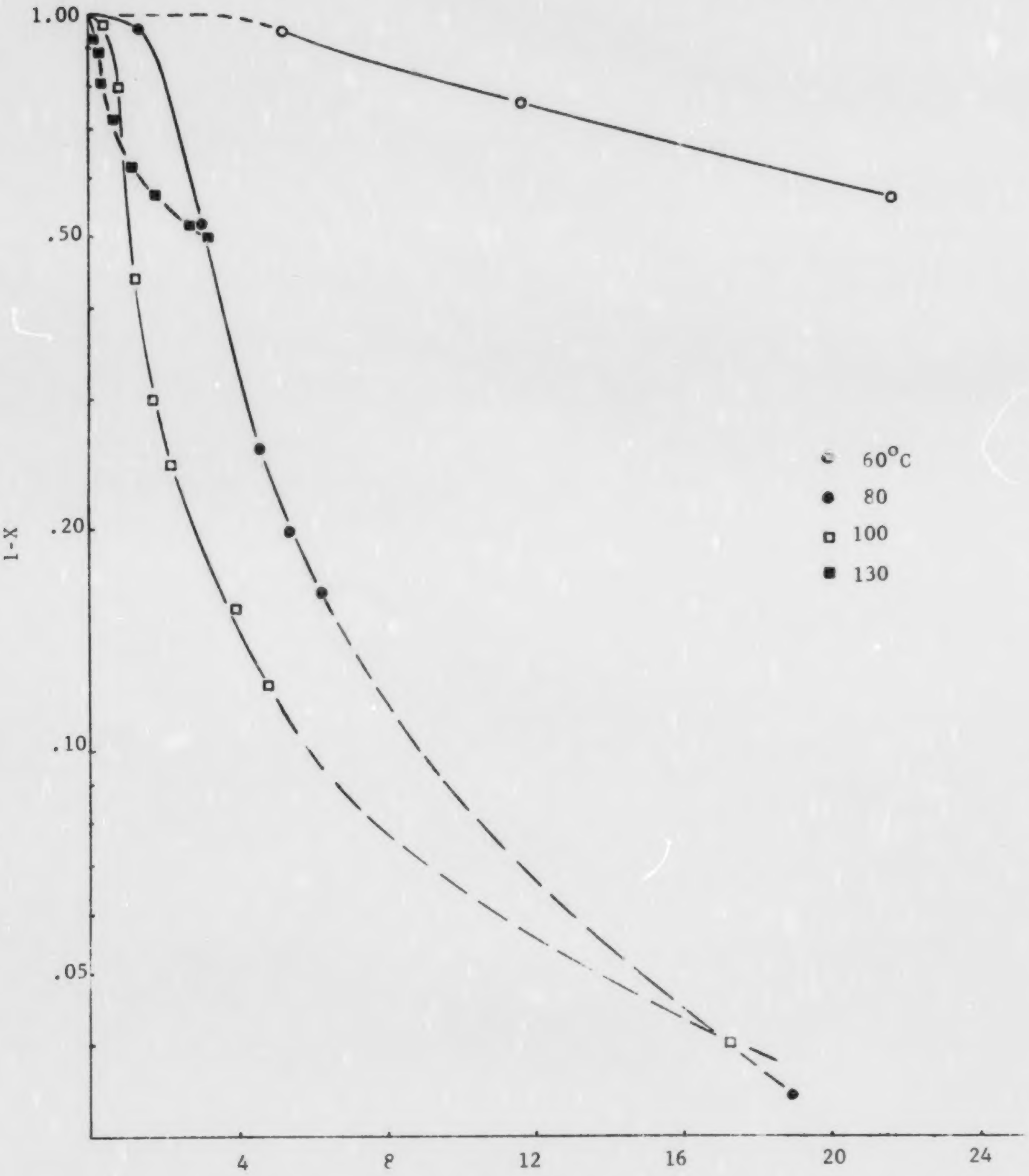
ABSOLUTE AROCLOR 1248 CONVERSION BASED ON FIRST ORDER KINETICS



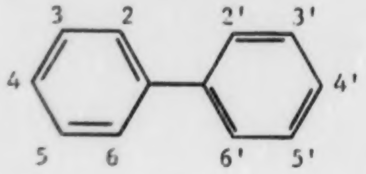
Time (arbitrary units)

Figure 3A-7

EXPERIMENTALLY OBSERVED AROCLOR 1248 KINETICS



isomers containing the same number of chlorine atoms per molecule, certain isomers were selectively produced and reacted. The conventional nomenclature is as follows:



For example consider all three ~~1~~ mono-chloro isomers. Figure (3A-8) are representative chromatograms of the ~~1~~ mono-chloro isomers vs chlorine conversion at 80°C and 50 atm H_2 pressure. The relative amount of the ortho substituted isomer increases with chlorine conversion whereas the ratio of the partially separated meta and para isomers is approximately constant. Figures (3A-9and10) are plots of the relative percentage of 2 and 2,2' di chloro biphenyls within each group of isomers having one and two chlorine atoms per biphenyl molecule respectively. In all cases the relative amount of ortho substituted material increases with chlorine conversion indicating that ortho substituted chlorine is less labile than meta and para substituted chlorine which are similar in reactivity.

An attempt was made to quantitate this behavior by assuming that any PCB mixture can be characterized by the degree of ortho vs combined meta + para substitution alone. First order rate expressions for the ortho 0 and meta + para MP reactions are

$$\frac{d0}{d\theta} = k_o 0$$

$$\frac{dMP}{d\theta} = k_{mp} MP$$

dividing these expressions we obtain

$$\frac{d0}{dMP} = \frac{k_o 0}{k_{mp} MP}$$

integrating gives

$$\frac{\log \frac{0}{0^o}}{\log \frac{MP}{MP^o}} = \frac{k_o}{k_{mp}}$$

Figure (3a-8)

DISTRIBUTION OF 1 CHLORO PCB ISOMERS AS A FUNCTION OF

CHLORINE CONVERSION X

50 ATM H_2 , 80°C , Ni on KIESELGUHR

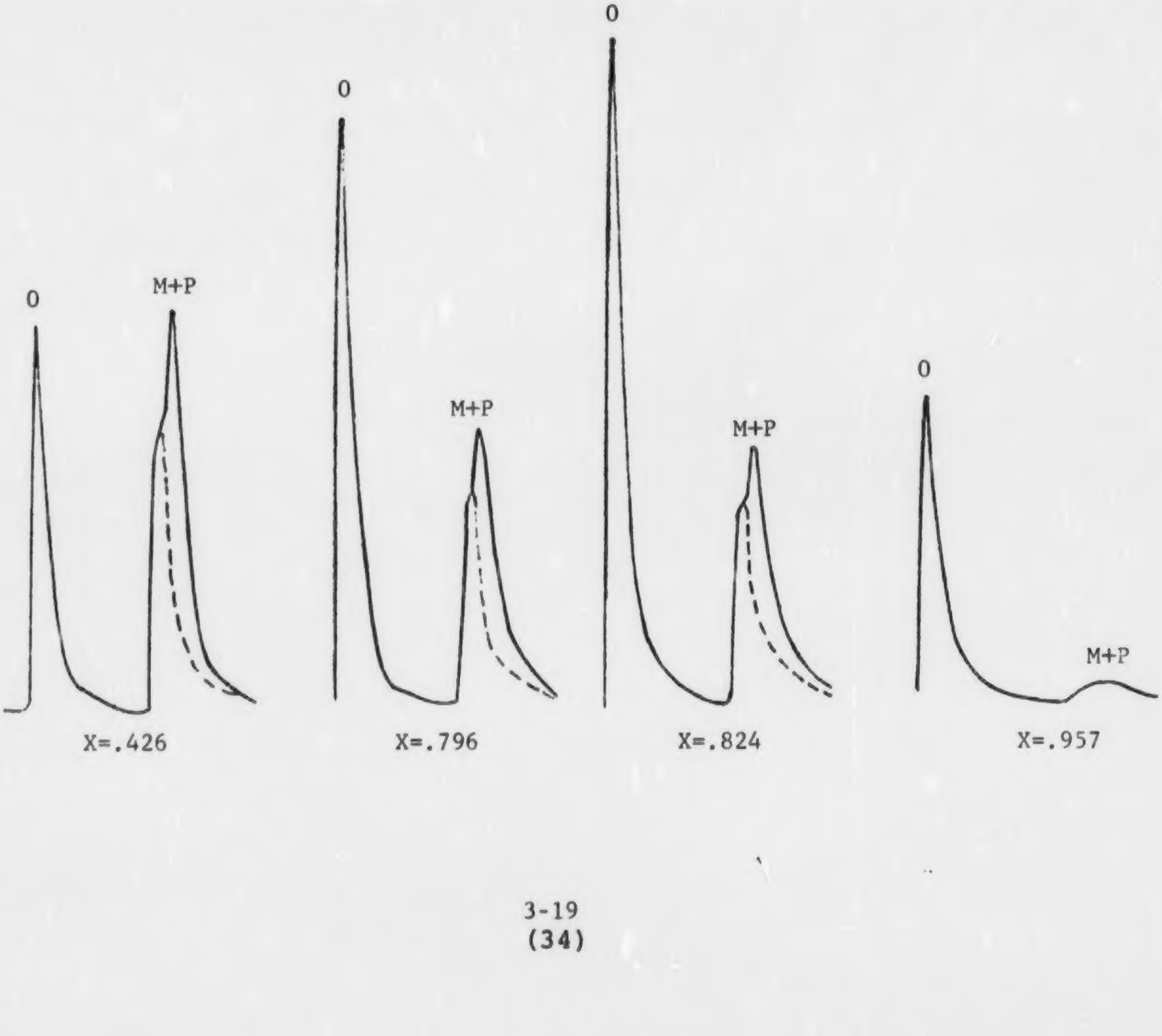


Figure (3a-9)

RELATIVE INCREASE OF ORTHO VS TOTAL MONOCHLORO BIPHENYL AS A FUNCTION OF CHLORINE CONVERSION X

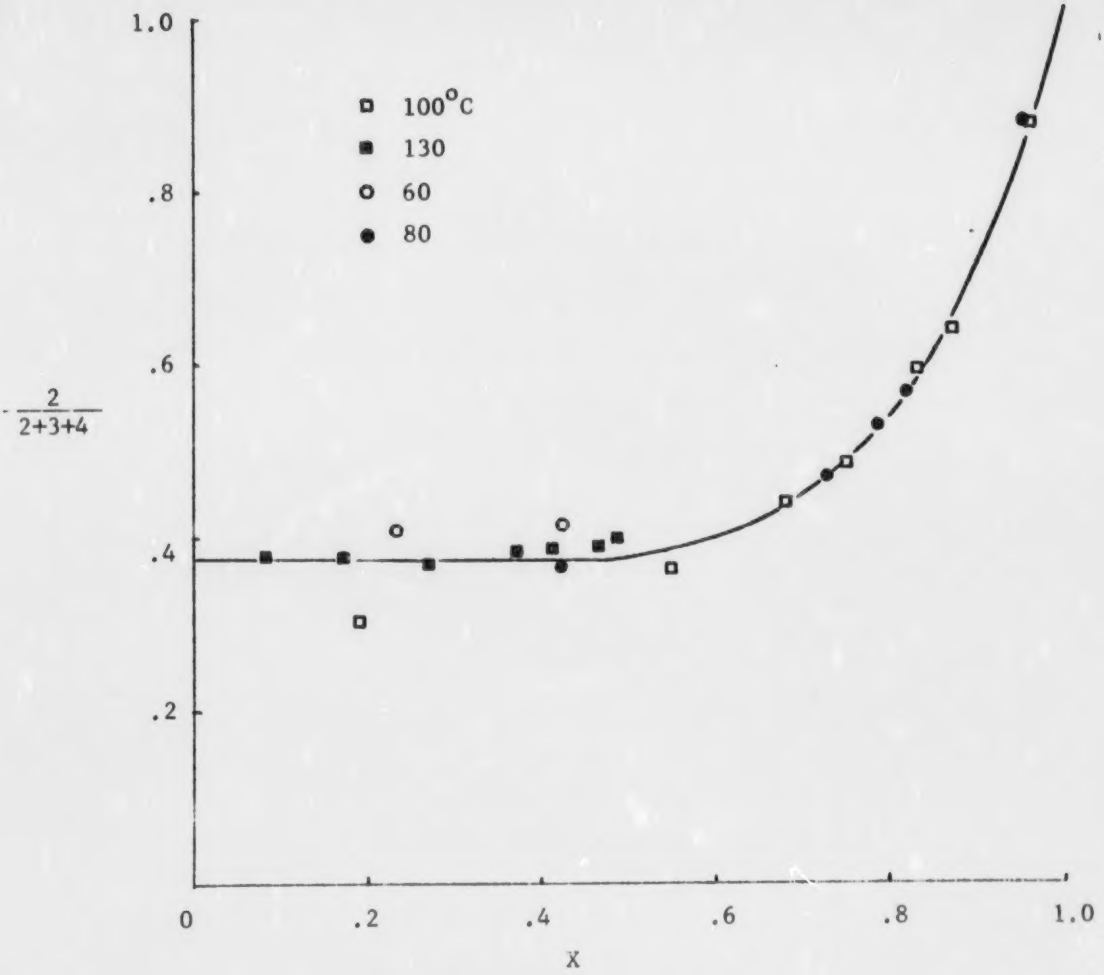
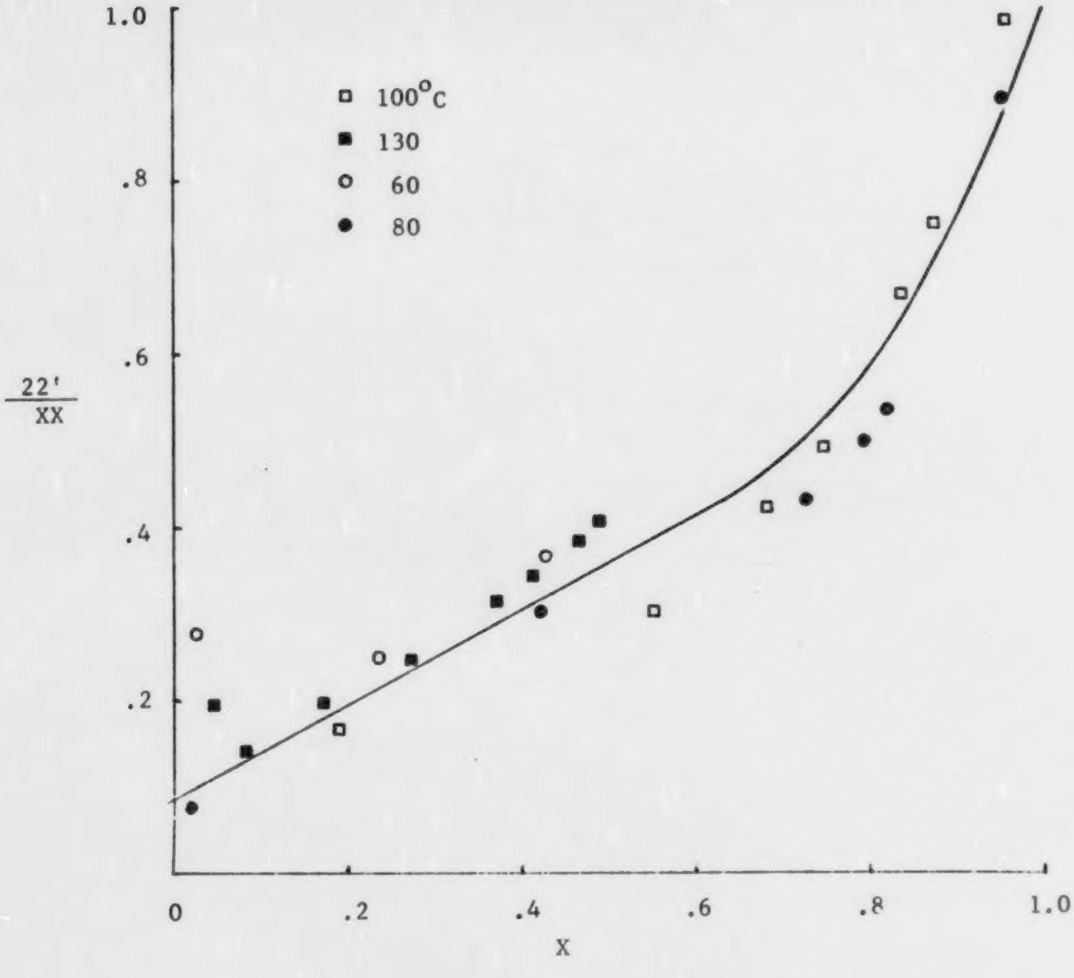


Figure (3a-10)

RELATIVE INCREASE OF 2,2' ISOMER VS TOTAL DICHLORO BIPHENYL AS A FUNCTION OF CHLORINE CONVERSION X



or a log log plot of $\frac{0}{0^{o}}$ vs $\frac{MP}{MP^{o}}$ should give a straight line with slope $\frac{k_o}{k_{mp}}$ see figure (3A-11). Table (3a-5) lists the % 0 and MP substitution values determined for experiments EPA 6,7,8 and 10 (see analytical section for details). Figure 9 shows that for the 60, 80, and 100°c experiments the valus of $\frac{k_o}{k_{mp}} = 0.52$ while for the 130° experiment where catalyst deactivation occured $\frac{k_o}{k_{mp}} = 0.31$.

Figure (3A-11)

AROCLOR 1248 HYDRODECHLORINATION AS CHARACTERIZED BY O VS M+P SUBSTITUTION

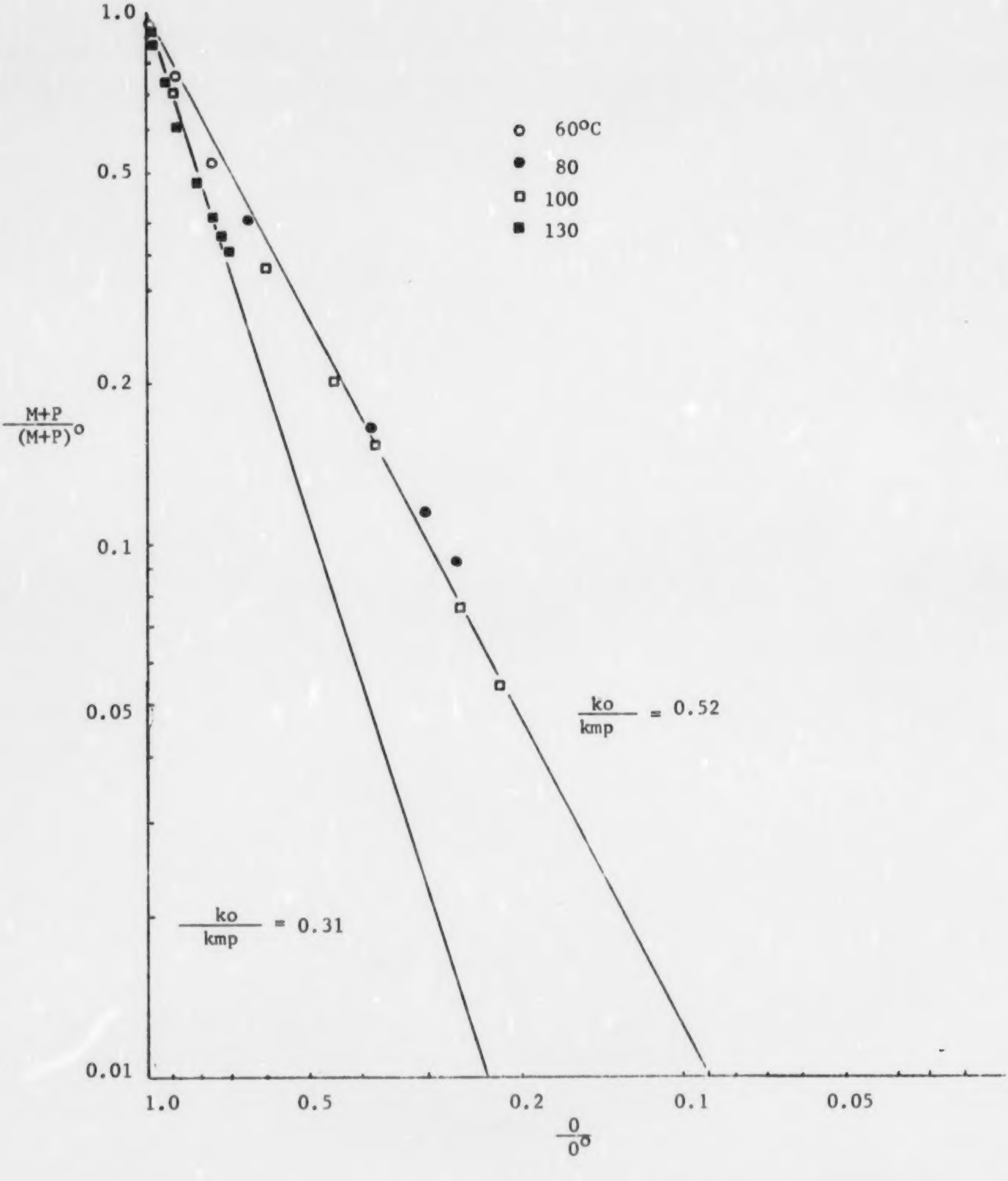


Table (3A-5)

N_i CATALYZED O VS MP PRODUCT DISTRIBUTIONS

		O		MP	O/O^o	MP/MP^o
Aroclor 1248	O^o =	1.6769	MP^o =	2.2413	1.000	1.0000
6-2		1.6856		2.1943	1.005	.9790
10-2		1.6891		2.1371	1.007	.9535
7-8		1.6701		2.1371	.996	.9535
8-1		1.6677		2.0625	.989	.9202
8-2		1.6431		1.9541	.980	.8719
8-3		1.5479		1.6576	.923	.740
6-3		1.5022		1.5824	.896	.706
7-9		1.4945		1.4862	.891	.663
8-5		1.4809		1.3664	.883	.610
8-7		1.3574		1.0699	.809	.477
8-9		1.2542		.9266	.748	.413
7-10		1.2798		.9477	.763	.423
8-11		1.2152		.8490	.725	.379
10-3		1.0879		.9184	.649	.410
8-12		1.1756		.7928	.701	.354
6-4		1.0100		.7425	.602	.331
6-5		.7532		.4579	.449	.204
10-4		.6411		.3741	.382	.167
6-6		.6296		.3461	.375	.154
10-5		.5076		.2543	.303	.113
10-6		.4447		.2089	.265	.0932
6-7		.4369		.1698	.261	.0758
6-8		.3699		.1212	.221	.0541
10-7		.1165		.0168	.0695	.0075
6-9		.1439		.0096	.0858	.0043

B. DDT, DDE, DDD

Screening tests were conducted in the pulse microreactor to study the thermal and catalytic reactions of DDT and DDD.

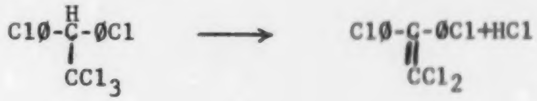
Detailed studies on DDE were undertaken in several liquid phase reactors using nickel and palladium catalysts at atmospheric and elevated pressures.

Continuous gas phase reactions were also carried out on DDE and DDD at higher temperatures than were feasible in the liquid phase reactors.

GAS PHASE PULSE MICROREACTOR SCREENING

Experiments were performed to determine the extent of thermal decomposition of DDT in the pulse microreactor. Half microliter samples of 9.5 wt% DDT in p-xylene were injected into the empty injector port. Heluim carrier gas flow rate was fixed at 30 cc /min while the temperature of the inlet was varied from 200°C to 360°C. DDE was identified as the major decomposition product by relative retention time.

In all cases the uncatalyzed reaction showed high selectivity to DDE by the following reaction.



$$Cl\phi-\overset{H}{\underset{CCl_3}{C}}-\phi Cl \longrightarrow Cl\phi-\underset{CCl_2}{\overset{}{C}}-\phi Cl + HCl \qquad (1)$$

Decomposition was not significant at temperatures below 190°C.

Two sets of experiments were carried out where 0.5μl samples of 5.2 wt% DDT (81%PP', 19%OP') and 5.1 wt% PP' DDD were reacted at 220°C, 2.3 atm. total pressure, and a residence time of approximately 0.01 sec based on carrier gas flow rate.

Each set consisted of six experiments. The first two investigated thermal reactions in the empty reactor with helium or hydrogen as the carrier gas. The last four experiments in each set used hydrogen as a carrier gas and a series of Pd on α-Al_2O_3 catalysts containing 0.00, 0.05, 0.10 and 0.35 wt% Pd.

Figures (3b-1,2) are log response chromatograms of products obtained in the

Figure (3b-1)

DDT HYDRODECHLORINATION

30 SCC/Min. Gas, 220 ± 10°C, 19 PSIG

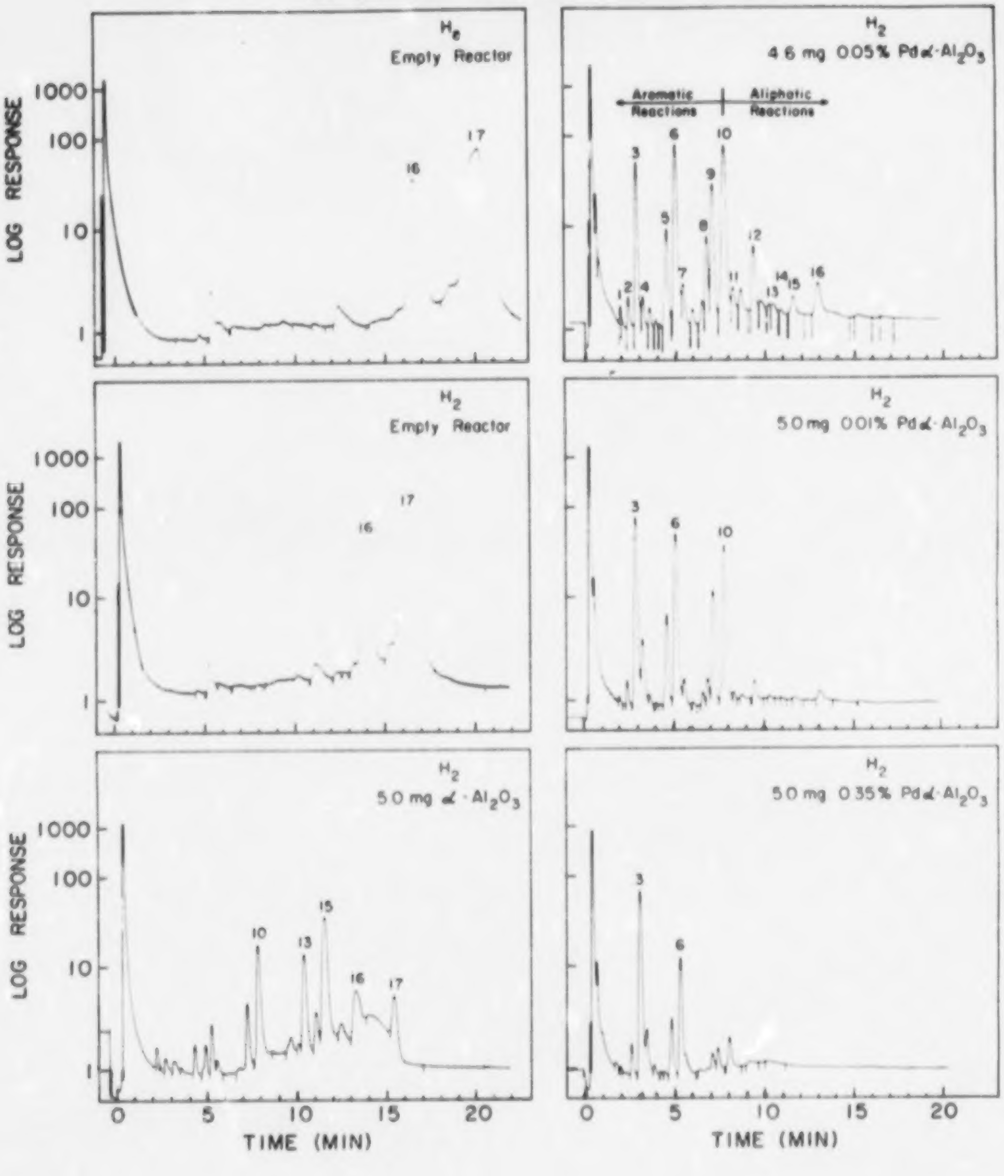
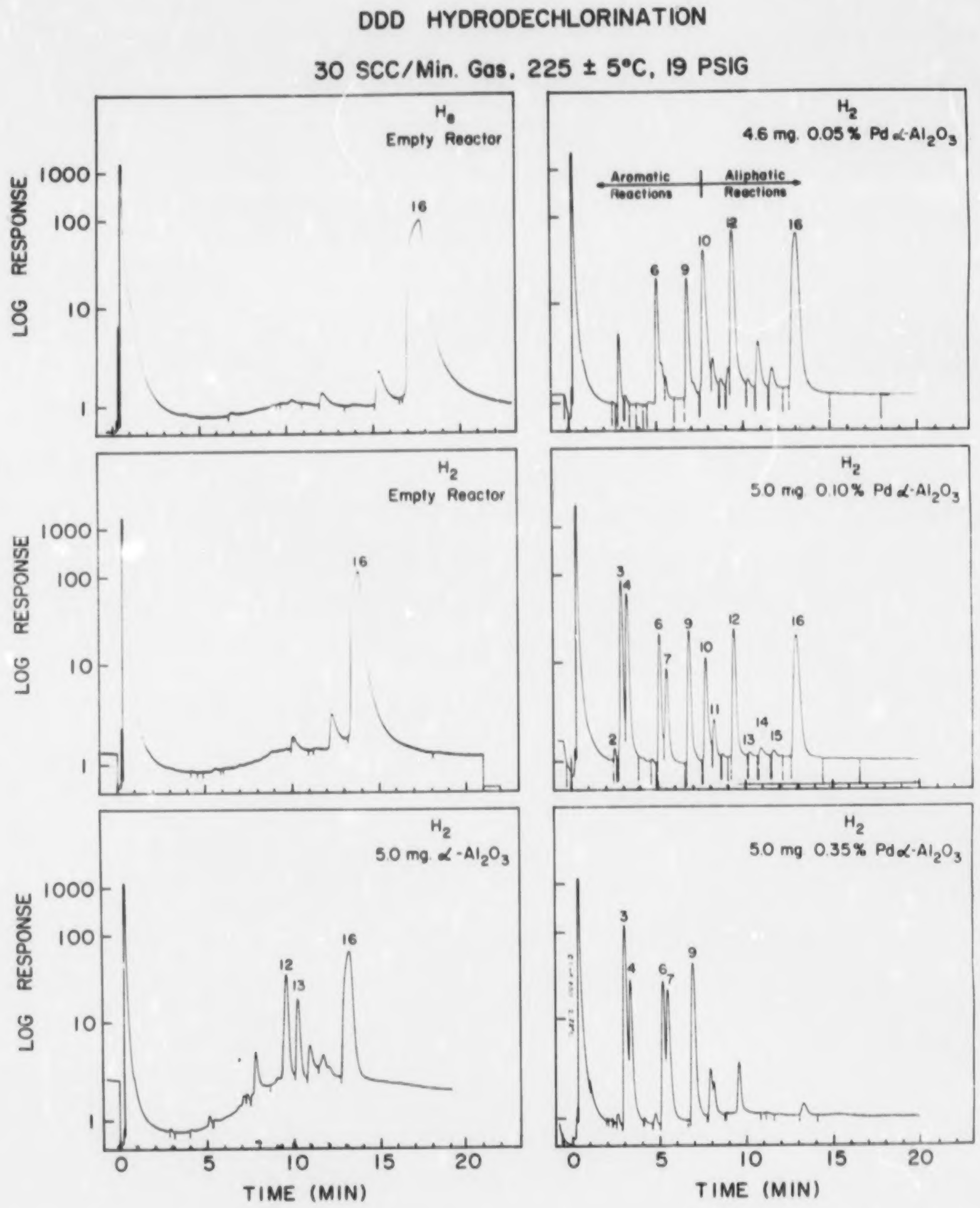


Figure (3b-2)



DDD HYDRODECHLORINATION

30 SCC/Min. Gas, 225 ± 5°C, 19 PSIG

DDT and DDD experiments respectively. Partial identification of major species produced is listed below and referenced numerically to Figures (3b-1,2).

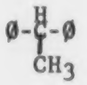
Compound #	Identification
3	1,1 diphenylethane
6	1p-chlorophenyl, 1-phenylethane
10	1,1 bis-parachlorophenylethane
15	p,p' DDE
16	o,p' DDT, P,P' DDD
17	p,p' DDT

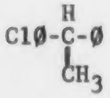
The DDT results, figure (3b-1), show that thermal reaction was minimal under these conditions but that α-Al_2O_3 alone catalyzed dehydrochlorination / hydrogenation reactions on the aliphatic portion of the molecule, with DDE,(15), being the major product. However aromatic hydrodechlorination was only catalyzed by Pd, with extent of aromatic hydrodechlorination dependent on metal loading.

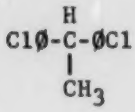
The DDD results, figure (3b-2), show similar lack of thermal reaction and dehydrochlorination by α-Al_2O_3 occured to a lesser extent. Product distributions were more complex indicating competitive rates of aromatic and aliphatic hydrodechlorination. DDD was generally less reactive than DDT at identical conditions. Based on these encouraging results extensive studies were carried out in the gas phase in a continuous flow reactor.

CONTINUOUS GAS PHASE EXPERIMENTS

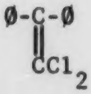
A series of reactions was carried out in the continuous gas phase reactor previously described. Five major DDE,(VI), hydrodechlorination reaction products, covering over 95% of the total products, were observed.

1.1 - biphenylethane  $\O\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}\O$ I

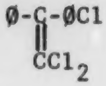
1 - chlorophenyl, 1 - phenylethane  $Cl\O\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}\O$ II

1,1 -bis-parachlorophenyl-ethane  III

$ClØ-\overset{H}{C}(CH_3)-ØCl$

1,1 biphenylethylene dichloride  IV

$Ø-C(=CCl_2)-Ø$

1-chlorophenyl, 1-phenylethylene dichloride  V

$Ø-C(=CCl_2)-ØCl$

We believe the trace components to be 1,1 biphenyl ethylenes containing 0,1, and 2 aromatic chlorines. Chlorine conversion was used as an extent of reaction parameter and is defined as $\frac{Ø_o - Ø}{Ø_o}$ where $Ø = \sum_{i=4}^{i=4} iCl_i$, $Ø_o$ is 4 based on the chlorine content of starting material, i=number of chlorines per molecule, and Cl_i = mole fraction of compounds having i chlorines per molecule. Tables (3b-1) and (3b-2) respectively list experimental conditions and product distributions for these experiments. Fig. (3b-3) shows the deactivation rate of the .35 wt% Pd on α -Alumina catalyst, by plotting total chlorine conversion vs time on stream (at T=200°C, P_{H_2} = 555 mmHg., P_{DDE} = 0.688 mmHg, and space time 0.0487 second.) A repeat experiment was done at identical conditions except for a slightly different amount of catalyst. These results are also shown on Figure (3b-3). This figure shows that the activity of freshly charged catalyst decreased very rapidly during the first 24 hours on stream. After that period the activity of the catalyst was much more stable. All kinetic data was taken after the catalyst had been on stream for more than one day. Figures (3b-4,5, and 6) are reaction paths obtained at 200°C and hydrogen pressures of 60 ± 20 mmHg, 140 ± 30 mmHg, and 580 ± 90 mmHg respectively while varying P_{DDE} from 0.255 to 0.966 mmHg and space time from 0.0244 to 0.0609 sec. Figs. (3b-7,8) are reaction paths obtained at hydrogen pressures of 580 ± 90 mmHg while temperatures were 230°C and 170°C respectively. The solid curves are a computer fit of the data as calculated from the reaction path model described later. Experiments were done in the continuous flow reactor at 200°C and 230°C respectively

TABLE (3b-1)

Continuous Flow Reactor Experimental Conditions

Run No.	100975	020876	021076
Catalyst	0	α-Al_2O_3	Catalyst used in 020876 regenerated at H_2 30 cc/min overnight
Weight (mg)	0	30.0	30.0
H_2 Flow Rate, gas $\frac{cc}{min}$	30	30	30
Total Gas Flow Rate Gas $\frac{cc}{min}$	30	30	30
Liquid Feed Rate Liq. $\frac{cc}{min}$	0.056	0.056	0.056
Temperature °C	200	200	230
Integral Samples (hrs)	#1 (0-2)	#1 (24-25) #2 (25-26)	#1 (24-25) #2 (25-26)
Remarks	No decomposition of DDE at 200°C was detected	No reaction of DDE with α-Al_2O_3 was detected at 200°C	No reaction of DDE with α-Al_2O_3 was detected at 230°C

TABLE (3b-1) (cont)

Continuous Flow Reactor Experimental Conditions

Run No.	112075	112275	112475
Catalyst	0.35 wt.% Pd on α-Al_2O_3	Catalyst used in 112075 regenerated at H_2 30 cc/min overnight	Catalyst used in 112275 regenerated at H_2 30 cc/min 12 hrs.
Weight (mg)	24.6	24.6	24.6
H_2 Flow Rate, gas $\frac{cc}{min}$ (hrs.)	30 (0-26) 7.79(26-29) 3.65(29-32) 8.70(32-35) 30(35-38)	60(0-1) 8.33(1-4) 6.12(4-7) 4.08(7-10)	30
Total Gas Flow Rate gas $\frac{cc}{min}$	30	60	30
Liquid Feed Rate, Liq. $\frac{cc}{min}$ (hrs.)	0.056	0.078	0.028 (0-13) 0.04 (13-16) 0.056 (16-19) 0.078 (18-22)
Temperature °C	200	200	200
Integral Samples (hrs.)	#2(25-26) #4(28-29) #6(31-32) #8(34-35) #10(37-38)	#2(0.5-1) #4(3.5-4) #6(6.5-7) #8(9.5-10)	#1(12-13) #2(15-16) #3(18-19) #4(21-22)

TABLE (3b-1) (cont)

Continuous Flow Reactor Experimental Conditions

Run No.	120375	120475	121375
Catalyst	Cat. used in 112475 regenerated at H_2 low flow rate several days	Cat. used in 120375 continue reaction at 0.02 cc/min liquid feed rate	0.35 wt.% Pd on α-Al_2O_3
Weight (mg)	24.6	24.6	28.9
H_2 Flow Rate, gas $\frac{cc}{min}$ (hrs.)	8.6	8.6	41.67
Total Gal Flow Rate, gas $\frac{cc}{min}$	35.7	35.7	41.67
Liquid Feed Rate, Liq. $\frac{cc}{min}$ (hrs.)	0.0201(0-25) 0.028 (25-28) 0.040(28-31) 0.056(31-34) 0.078(34-37)	0.02(37-50) 0.028(50-53) 0.11(53-56)	0.056(0.25) 0.11(25-28) 0.04(28-31) 0.078(31-34) 0.028(34-37)
Temperature °C	200	200	170
Integral samples (hrs.)	#1(24-25) #2(27-28) #3(30-31) #4(33-34) #5(36-37)	#3(55-56)	#1(24-25) #2(27-28) #3(30-31) #4(33-34) #5(36-37)

TABLE (3b-1) (cont)

Continuous Flow Reactor Experimental Conditions

Run No.	121475	121575	011476
Catalyst	Cat. used in 121375 overnight reaction at 200°C and 0.028 cc/min liquid rate	Cat. used in 121475 overnight reaction at 230°C and 0.028 cc/min liquid rate	0.35 wt.% Pd on α-Al_2O_3
Weight (mg)	28.9	28.9	28.9
H_2 Flow Rate, gas $\frac{cc}{min}$ (hrs.)	41.67	41.67	30
Total Gas Flow rate, gas $\frac{cc}{min}$	41.67	41.67	30
Liquid Feed Rate, Liq. $\frac{cc}{min}$ (hrs.)	0.028 (37-50) 0.11 (50-53) 0.04 (53-56) 0.078 (56-59) 0.056 (59-62)	0.028 (62-74) 0.11 (74-77) 0.04 (77-80) 0.078 (80-83) 0.056 (83-86)	0.056 (0-8) 0.028 (8-24) 0.04 (24-27) 0.056 (27-30) 0.078 (30-33)
Temperature °C	200	230	170
Integral Samples (hrs.)	#1 (49-50 #2 (52-53) #3 (55-56) #4 (58-59) #5 (61-62)	#1 (73-74) #2 (76-77) #3 (79-80) #4 (82-83) #5 (85-86)	#1 (23-24) #2 (26-27) #3 (28-30) #4 (32-33)

TABLE (3b-1) (cont)

Continuous Flow Reactor Experimental Conditions

Run No.	011576	012176	012276
Catalyst	Cat. used in 011476 overnight reaction at 230°C and 0.028 liquid feed rate	0.35 wt.% Pd on α-Al_2O_3	Cat. used in 012176 overnight reaction at 200°C and 0.028 cc/min liquid feed rate
Weight (mg)	28.9	27.1	27.1
H_2 Flow Rate, gas $\frac{cc}{min}$ (hrs).	30	30	30
Total Gas Flow Rate, gas $\frac{cc}{min}$	30	30	30
Liquid Feed Rate, Liq. $\frac{cc}{min}$ (hrs.)	0.028 (33-48) 0.04 (48-51) 0.056 (51-54) 0.078 (54-57)	0.056 (0-24) 0.028 (24-48) 0.04 (48-51) 0.056 (51-54) 0.078 (54-57)	0.028 (57-73) 0.04 (73-76) 0.056 (76-79) 0.078 (79-82)
Temperature °C (hrs.)	230	200 (0-24) 170 (24-57)	200 (57-82)
Integral Samples (hrs.)	#1 (47-48) #2 (50-51) #3 (53-54) #4 (56-57)	#1 (47-48) #2 (50-51) #3 (53-54) #4 (56-57)	#1 (72-73) #2 (75-76) #3 (78-79) #4 (81-82)

TABLE (3b-1)(cont)

Continuous Flow Reactor Experimental Conditions

Run No.	012376
Catalyst	Cat. used in 012276 overnight reaction at 230°C and 0.028 cc/min liquid feed rate
Weight (mg)	27.1
H_2 Flow Rate, gas $\frac{cc}{min}$ (hrs.)	30
Total Gas Flow Rate, gas $\frac{cc}{min}$	30
Liquid Feed Rate, Liq. $\frac{cc}{min}$ (hrs.)	0.028 (82-96) 0.04 (96-99) 0.056 (99-102) 0.078 (102-105)
Temperature °C (hrs.)	230 (82-105)
Integral Samples (hrs.)	#1 (95-96) #2 (98-99) #3 (101-102) #4 (104-105)

TABLE (3b-2)

Analysis Results

Product Distribution and Chlorine Conversion

Mole %	Run No.	112075 #2	#4	#6	#8	#10	112275 #2
I		0.1276	0.0822	0.0250	0.0342	0.0859	0.1912
II		0.3687	0.3019	0.1741	0.2115	0.3187	0.3766
III		0.2531	0.2113	0.1830	0.2170	0.2354	0.2396
IV		0.0081	0.0221	0.0202	0.0198	0.0185	0.0061
V		0.0762	0.1241	0.1700	0.1547	0.1072	0.0534
VI		0.1655	0.2583	0.4278	0.3628	0.2344	0.1331
Cl Conv. %		55.46	45.65	29.96	34.99	47.86	60.99

Mole %	Run No.	112275 #4	#6	#8	112475 #1	#2	#3
I		0.0528	0.0167	0	0.3708	0.2431	0.2008
II		0.2252	0.1327	0.0671	0.3649	0.3738	0.3551
III		0.1715	0.1589	0.1187	0.1428	0.1810	0.1906
IV		0.0216	0.0155	0.0109	0.0063	0.0092	0.0095
V		0.1512	0.1668	0.1780	0.0412	0.0576	0.0663
VI		0.3796	0.5094	0.6254	0.0739	0.1353	0.1778
Cl Conv. %		35.42	24.51	15.95	72.94	63.30	58.37

TABLE (3b-2)(cont)

Analysis Results Product Distribution and Chlorine Conversion

Mole %	Run No.	112475	120375				
		#4	#1	#2	#3	#4	#5
I		0.0999	0.3882	0.2654	0.1431	0.0735	0.0326
II		0.3133	0.3532	0.3693	0.3380	0.2500	0.1849
III		0.2320	0.1258	0.1654	0.2097	0.2372	0.2137
VI		0.0121	0.0079	0.0088	0.0132	0.0146	0.0153
V		0.0858	0.0387	0.0531	0.0747	0.0975	0.1264
VI		0.2569	0.0863	0.1379	0.2212	0.3271	0.4231
Cl Conv. %		47.84	72.95	64.29	52.68	41.13	32.14

Mole %	Run No.	120475	121375				
		#3	#1	#2	#3	#4	#5
I		0.0091	0	0	0	0	0
II		0.0993	0.0146	0	0	0	0.0090
III		0.1603	0.2312	0.0692	0.1617	0.0863	0.1826
IV		0.0108	0	0	0	0	0
V		0.1389	0.0705	0.0338	0.0573	0.0391	0.0638
VI		0.5816	0.6837	0.8970	0.7810	0.8747	0.7447
Cl Conv. %		20.39	14.42	4.31	9.51	5.29	11.40

TABLE (3b-2)(cont)

Analysis Results Product Distribution and Chlorine Conversion

		121475					121575
Mole %	Run No.	#1	#2	#3	#4	#5	#1
I		0	0	0	0	0	0.0529
II		0.1281	C.C081	0.0397	0.0114	0.0195	0.2538
III		0.4099	0.1406	0.2694	0.1631	0.1969	0.2809
IV		0.0068	0	0.0021	0	0	0.0171
V		0.1081	0.0543	0.0895	0.0628	0.0752	0.1125
VI		0.3470	0.7969	0.5993	0.7627	0.7084	0.2827
Cl Conv. %		33.16	9.01	18.79	10.58	13.19	42.05

		121575				011476	
Mole %	Run No.	#2	#2	#4	#5	#1	#2
I		0	0.0155	0	0	0	0
II		0.0237	0.1357	0.0358	0.0624	0.1230	0.0767
III		0.1578	0.2512	0.1751	0.1994	0.5255	0.4498
IV		0.0036	0.0118	0.0041	0.0063	0.0050	0
V		0.0771	0.1183	0.0912	0.1039	0.1131	0.1103
VI		0.7376	0.4675	0.6845	0.6279	0.2333	0.3631
Cl Conv. %		11.80	27.84	14.86	17.57	38.59	31.01

TABLE (3b-2)(cont)

Analysis Results Product Distribution and Chlorine Conversion

		011476		011576			
Mole %	Run No.	#3	#4	#1	#2	#3	#4
I		0	0	0.2401	0.1513	0.0851	0.0289
II		0.0244	0.0130	0.4637	0.4306	0.3557	0.2037
III		0.3159	0.1544	0.1573	0.2135	0.2487	0.2534
IV		0	0	0.0252	0.0277	0.0272	0.0194
V		0.0980	0.0583	0.0568	0.0912	0.1224	0.1502
VI		0.5618	0.7743	0.0569	0.0857	0.1610	0.3444
Cl Conv. %		20.07	10.15	69.33	61.77	52.03	35.56

		012176				012276	
Mole %	Run No.	#1	#2	#3	#4	#1	#2
I		0	0	0	0	0.0093	0.0037
II		0.0385	0.0197	0.0054	0	0.1490	0.0811
III		0.3579	0.2672	0.1601	0.0908	0.3878	0.3447
IV		0	0	0	0	0.0091	0.0042
V		0.0938	0.0823	0.0602	0.0420	0.1166	0.1066
VI		0.5097	0.6309	0.7744	0.8672	0.3282	0.4596
Cl Conv. %		23.14	16.89	9.91	5.59	34.87	26.57

TABLE (3b-2)(cont)

Analysis Results Product Distribution and Chlorine Conversion

Mole %	Run No.	012276 #3	#4	012376 #1	#2	#3	#4
I		0	0	0.0591	0.0228	0.0018	0
II		0.0413	0.0186	0.2969	0.2032	0.1281	0.0614
III		0.3009	0.1918	0.2864	0.2897	0.2595	0.2059
IV		0.0033	0	0.0221	0.0171	0.0116	0.0064
V		0.0958	0.0728	0.1221	0.1383	0.1253	0.1013
VI		0.5544	0.7168	0.2134	0.3289	0.4737	0.6251
Cl Conv. %		21.13	12.81	46.66	36.32	26.48	17.74

Figure (3b-3)

Deactivation of .35 wt.% Pd on α-Al_2O_3

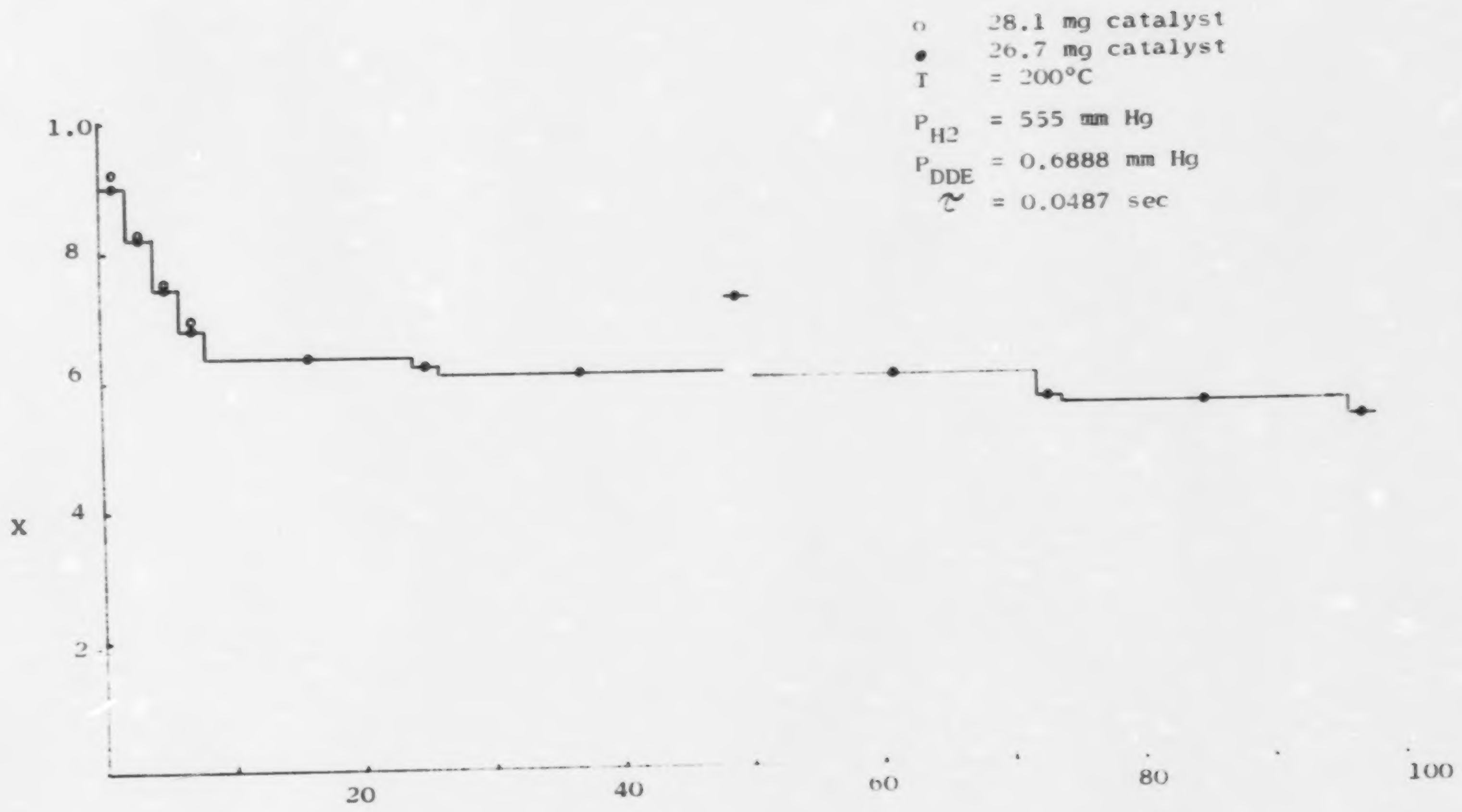


FIGURE (3b-4)

SELECTIVITY PLOT

$T = 200^{\circ}C$

$P_{H_2} = 60 \pm 20$ mm Hg

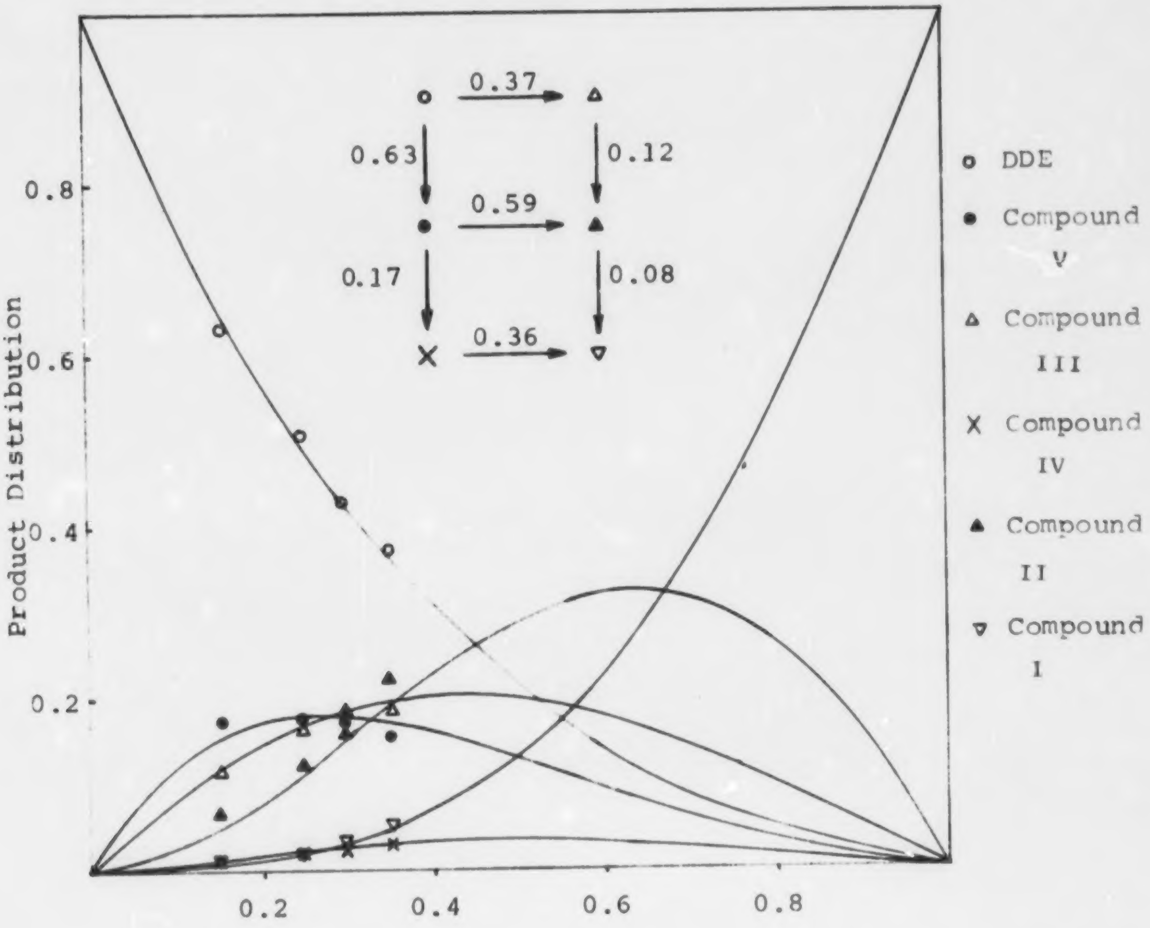


FIGURE (3b-5)

SELECTIVITY PLOT

T = 200°C

P_{H_2} = 140±30 mm Hg

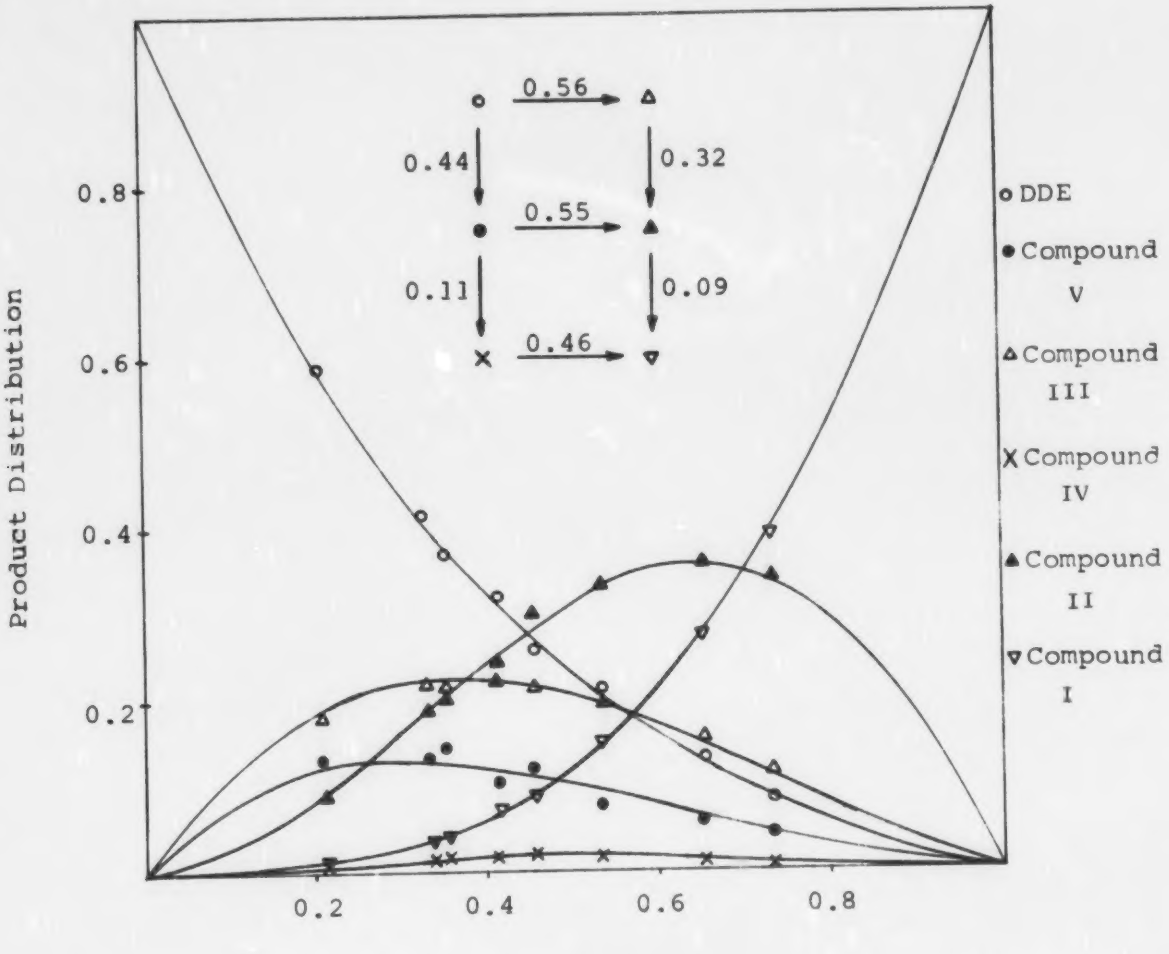


FIGURE (3b-6)

SELECTIVITY PLOT

$T = 200^{\circ}C$

$P_{H_2} = 580 \pm 90$ mm Hg

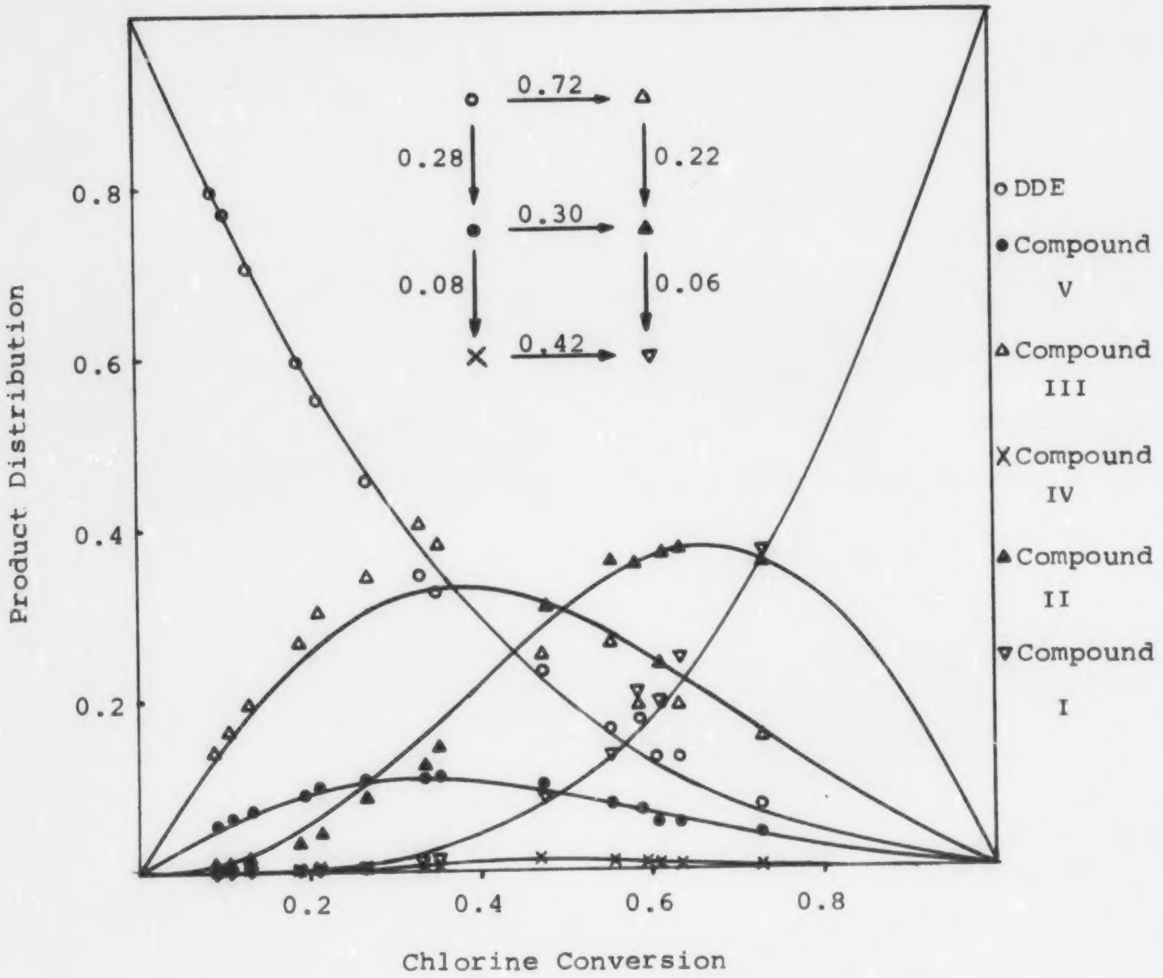


FIGURE (3b-7)

SELECTIVITY PLOT

$T = 230^{\circ}C$

$P_{H_2} = 580 \pm 90$ mm Hg

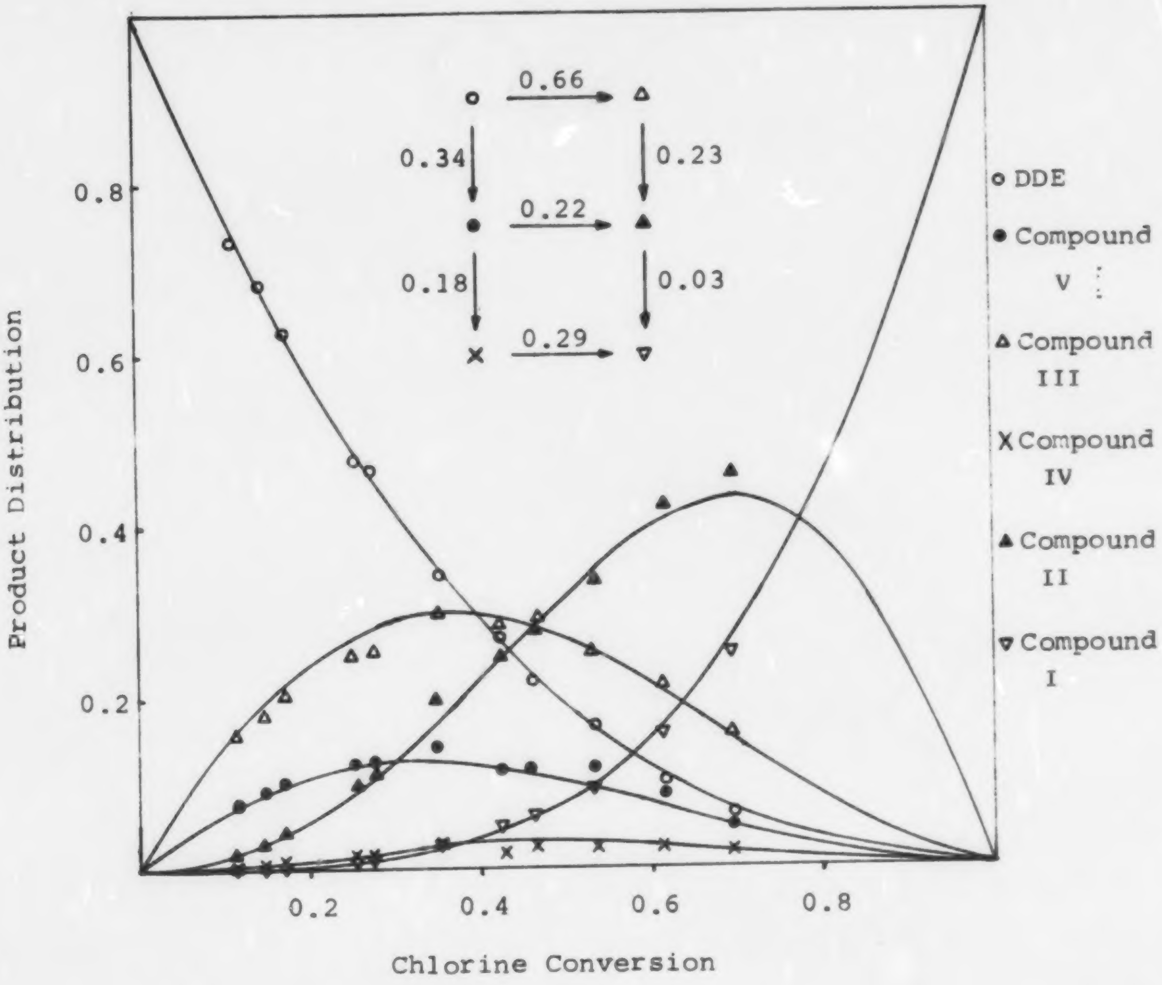
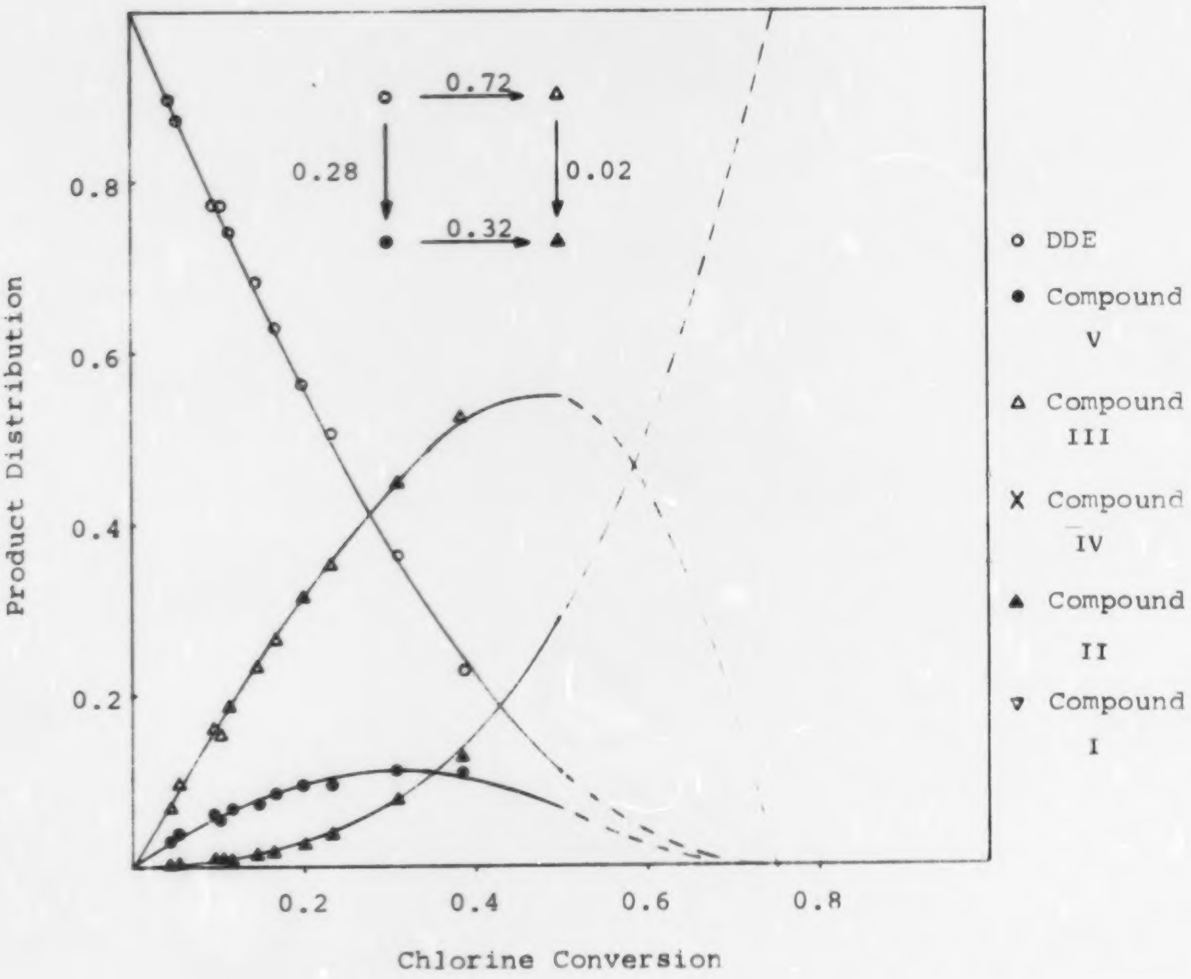


FIGURE (3b-8)

SELECTIVITY PLOT

$T = 170^{\circ}C$

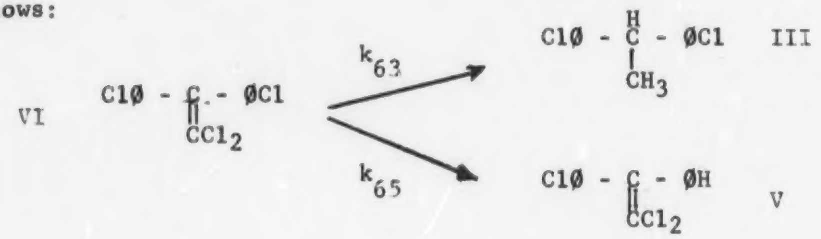
$P_{H_2} = 580 \pm 90$ mm Hg



Remarks: No Compounds $\overline{IV}$ and $\overline{VI}$ were found

Model was limited to 75% conv.

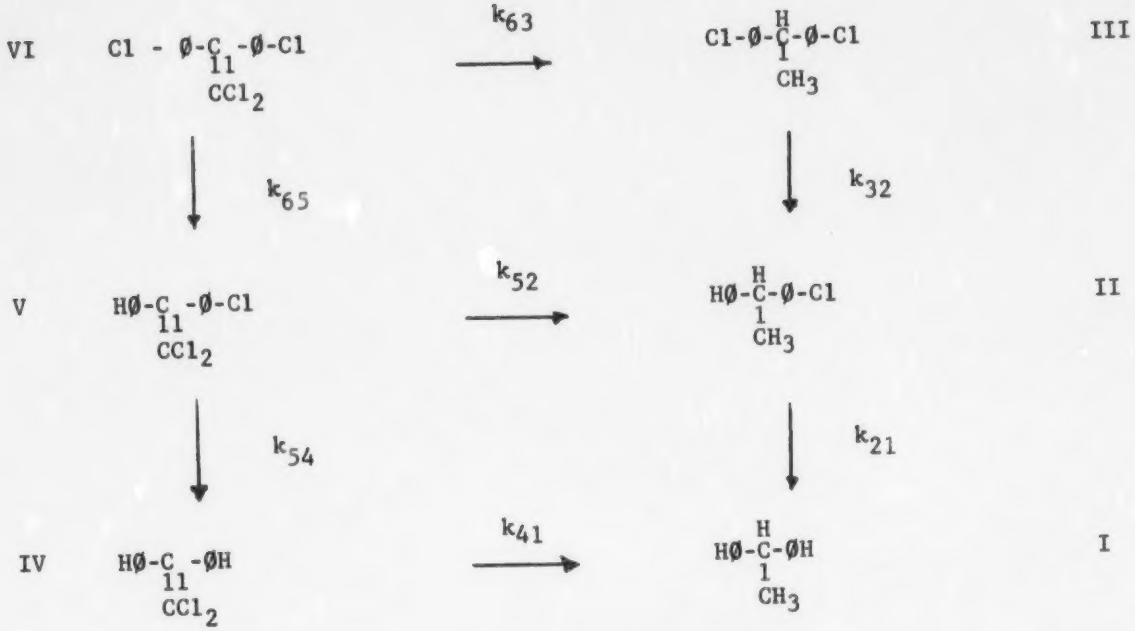
(P_{H_2} = 555 mmHg, P_{DDE} = 0.688 mmHg and space time 0.0487 second) with α - Al_2O_3 alone in order to determine the effect of the catalyst support. The results show that there was essentially no reaction of DDE over α - Al_2O_3. In contrast figs. (3b-1,2) of the pulse microreactor results show that α - Al_2O_3 has dehydrochlorination / hydrogenation activity across the aliphatic part of DDT and DDD molecules. The reaction paths, Figures (3b-4,5,6,7, and 8), show that at low conversion both species III and IV are initial products indicating parallel reactions occur. Therefore the first step in the hydrodechlorination of DDE is as follows:



$$\text{VI}\quad Cl\phi - \underset{\overset{\|}{CCl_2}}{C} - \phi Cl \xrightarrow{k_{63}} Cl\phi - \underset{CH_3}{\overset{H}{C}} - \phi Cl \quad \text{III} \qquad (2)$$

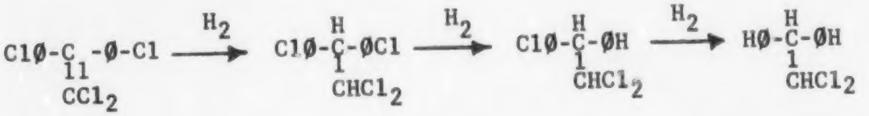
$$\text{VI}\quad Cl\phi - \underset{\overset{\|}{CCl_2}}{C} - \phi Cl \xrightarrow{k_{65}} Cl\phi - \underset{\overset{\|}{CCl_2}}{C} - \phi H \quad \text{V} \qquad (3)$$

Reaction 2 involves the concerted removal of two olefinic chlorines and rapid hydrogenation of the dechlorinated olefin. The fact that only trace olefinic intermediates were observed may also indicate the existence of a non-equilibrium adsorption-desorption sequence. Later reaction steps were characterized by consecutive removal of aromatic chlorine. The product of reaction (2) still has an aromatic chlorine and both olefinic chlorines so that further hydrodechlorination may proceed in parallel. The complete reaction scheme to describe DDE hydrodechlorination is as follows:



$$\begin{tikzcd}
\text{VI}\quad \mathrm{Cl\text{-}\emptyset\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\emptyset\text{-}Cl} \arrow[r, "k_{63}"] \arrow[d, "k_{65}"] & \mathrm{Cl\text{-}\emptyset\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\emptyset\text{-}Cl}\quad \text{III} \arrow[d, "k_{32}"] \\
\text{V}\quad \mathrm{H\emptyset\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\emptyset\text{-}Cl} \arrow[r, "k_{52}"] \arrow[d, "k_{54}"] & \mathrm{H\emptyset\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\emptyset\text{-}Cl}\quad \text{II} \arrow[d, "k_{21}"] \\
\text{IV}\quad \mathrm{H\emptyset\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\emptyset H} \arrow[r, "k_{41}"] & \mathrm{H\emptyset\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\emptyset H}\quad \text{I}
\end{tikzcd}$$

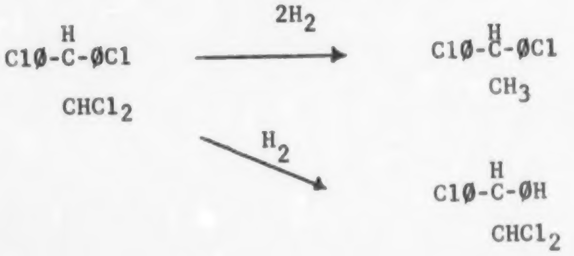
Initial hydrogenation of DDE did not occur since there were no intermediates found such as VII, VIII and IX in the following equation.



$$\mathrm{Cl\emptyset\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\emptyset\text{-}Cl} \xrightarrow{H_2} \mathrm{Cl\emptyset\text{-}\overset{H}{\underset{\underset{CHCl_2}{|}}{C}}\text{-}\emptyset Cl} \xrightarrow{H_2} \mathrm{Cl\emptyset\text{-}\overset{H}{\underset{\underset{CHCl_2}{|}}{C}}\text{-}\emptyset H} \xrightarrow{H_2} \mathrm{H\emptyset\text{-}\overset{H}{\underset{\underset{CHCl_2}{|}}{C}}\text{-}\emptyset H} \qquad (4)$$

VII VIII IX

Intermediate VII is DDD which was the only homologous intermediate chlorine compound commercially available. One seperate experiment has been done on DDD hydrodechlorination at 200°C ($Ph_2 = 650 \pm 50$mmHg) by varying P_{DDD} from 0.214mmHg to 0.529mmHg and space time from 0.0582 to 0.0674 second. Intermediate VIII and IX were indeed observed. The corresponding reaction path is shown on Fig. (3b-9). The first step of DDD hydrodechlorination is then as follows.

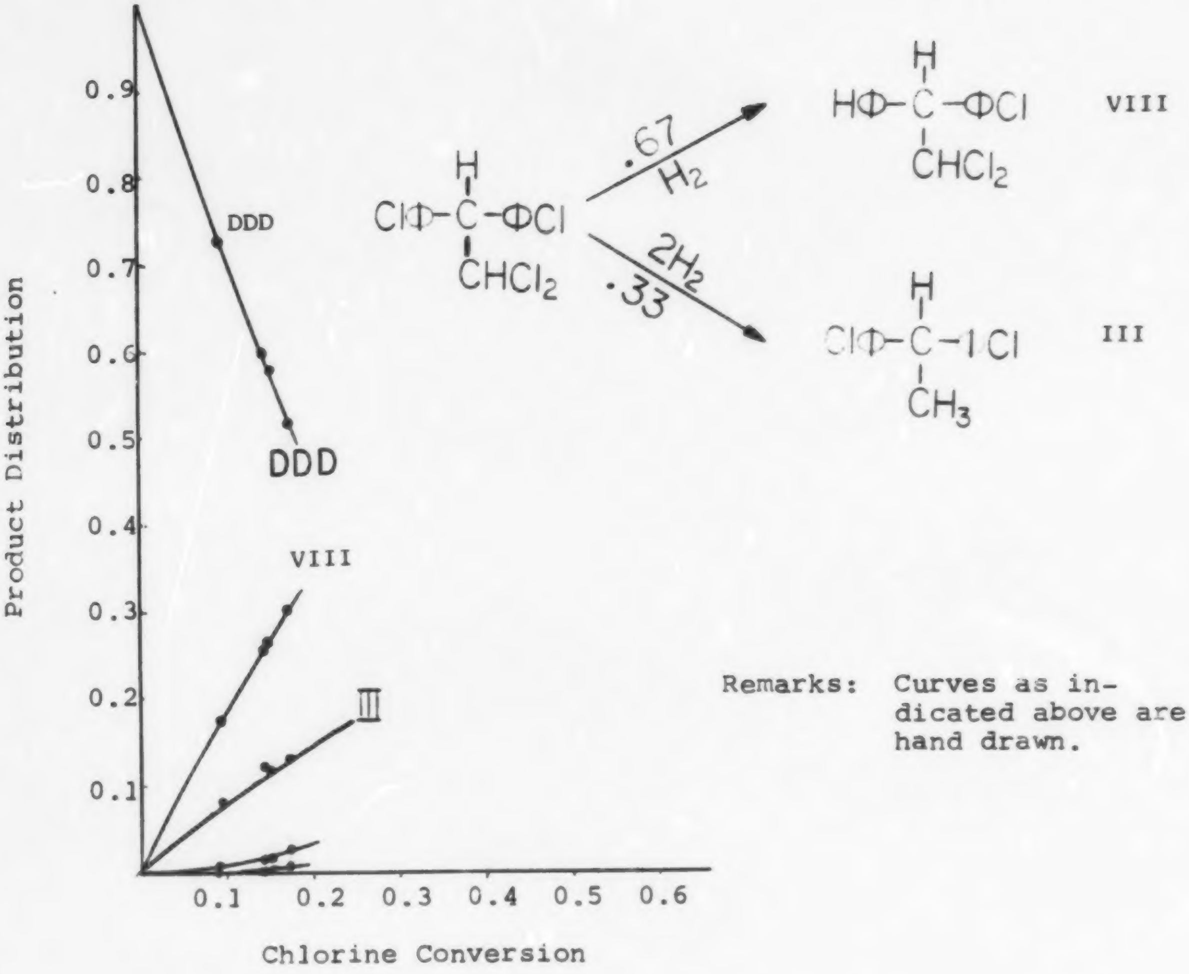


$$\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CHCl_2}{C}}\text{-}\emptyset Cl} \xrightarrow{2H_2} \mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}\emptyset Cl} \qquad (5)$$

$$\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CHCl_2}{C}}\text{-}\emptyset Cl} \xrightarrow{H_2} \mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CHCl_2}{C}}\text{-}\emptyset H} \qquad (6)$$

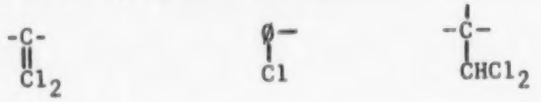
FIGURE (3b-9)

DDD SELECTIVITY PLOT



Remarks: Curves as indicated above are hand drawn.

Again reaction (5) is a one step reaction without intermediate desorption. Another comparison between DDE and DDD hydrodechlorination is based on reactivity. At the same experimental conditions as stated above the DDE reaction had approximately 20% more total chlorine conversion that the DDD reaction. The difference between DDE and DDD is the presence of olefinic vs aliphatic chlorine. This fact plus the observation that olefinic chlorines are more reactive than aromatic chlorines gives the following reactivity order for hydrodechlorination in the DDE, DDD series.



$$\underset{Cl_2}{\overset{\|}{-C-}} \qquad \underset{Cl}{\overset{|}{\phi-}} \qquad \underset{CHCl_2}{\overset{|}{-\overset{|}{C}-}}$$

← ?

more reactive ⟶ less reactive

This observation is in agreement with those reported by Kammerer, Horner, Freifelder, and Weiss (see Section 2) that olefinic chlorines are more reactive than aliphatic chlorines in catalytic hydrodechlorination.

Based on the reaction scheme as shown a set of rate equations was written in order to find the relative rate constants of each step based on two assumptions:

1. The reactor is essentially backmixed. Calculation of the degree of dispersion in the continuous flow reactor showed that the vessel dispersion number $\frac{D}{UL}$ (D axial dispersion coefficient, U velocity, L length of catalyst bed) is 0.25. This degree of dispersion is far from the limiting plug flow condition and is considerably closer to the backmixed limit. Furthermore the standard deviation was less for correlation of the data with the backmixed model and the location of the maximum concentration of intermediate species on the reaction path diagram was better described by this model. The assumption of backmixing was justified (though not proved) by these three measures. 2. Langmuir - Hinshelwood kinetics describe the reaction system and first order functionality describes the relative rates in a manner similar to that used for Aroclor 1248. Hydrogen functionality terms are incorporated into the rate constants.

$$r_{VI} = -(k_{65} + k_{63})\ VI$$

$$r_V = k_{65}\ VI - (k_{54} + k_{52})\ V$$

$$r_{IV} = k_{54}\ V - k_{41}\ IV$$

$$r_{III} = k_{63}\ VI - k_{32}\ III$$

$$r_{II} = k_{32}\ III + k_{52}\ V - k_{21}\ II$$

$$r_I = k_{21}\ II + k_{41}\ IV$$

Define relative rates:

$$r_V^* = \frac{rV}{rVI}\ ,\quad r_{IV}^* = \frac{rIV}{r_{VI}}\ ,\quad r_{III}^* = \frac{r_{III}}{r_{VI}}\ ,\quad r_{II}^* = \frac{r_{II}}{r_{VI}}\ ,\ \text{and}\ \ r_I^* = \frac{r_I}{r_{VI}}$$

$$\text{and}\quad V^* = \frac{V}{VI}\ ,\quad IV^* = \frac{IV}{VI}\ ,\quad III^* = \frac{III}{VI}\ ,\quad II^* = \frac{II}{VI}\ ,\ \text{and}\ \ I^* = \frac{I}{VI}$$

also define relative rate constants:

$$a = \frac{k_{65}}{k_{65}+k_{63}} \qquad d = \frac{k_{63}}{k_{65}+k_{63}} \qquad b = \frac{k_{52}}{k_{65}+k_{63}} \qquad e = \frac{k_{32}}{k_{65}+k_{63}}$$

$$c = \frac{k_{54}}{k_{65}+k_{63}} \qquad g = \frac{k_{21}}{k_{65}+k_{63}} \qquad f = \frac{k_{41}}{k_{65}+k_{63}}$$

then:

$$r_V^* = a - (b+c)\ V^*$$

$$r_{III}^* = d - e\ III^*$$

$$r_{IV}^* = cV^* - \quad IV^*$$

$$r_{II}^* = eIII^* + bV^* - gII^*$$

$$r_I^* = \quad IV^* + gII^*$$

and $a+d = 1$

From a plot of r_V^* vs V^* a and b+c were obtained. From a plot of r_{III}^* vs III^* d and e were obtained. Finally from a plot of r_V^* vs II^* g was obtained, if f $IV^* \simeq 0$

The rest of the relative rate constants were estimated by observation of the data. Based on these rate constants, product distribution and chlorine conversion could be calculated and matched with the experimental results. Adjustment of the rate constants was necessary in order to get the best fit with the experimental data. The final relative rate constants for DDE hydrodechlorination are shown on Fig. (3b-10). All of the values are relative to $(k_{65}+k_{63})$. The solid lines on Figures (3b-4,5,6,7, and 8) are calculated reaction paths based on these constants. At 170°C I and IV were not observed, therefore, the model is applied only up to 75% conversion.

Fig. (3b-10) shows that temperature changes from 170°C to 230°C did not appreciably affect the relative rates of olefinic and aromatic hydrodechlorination reactions of DDE, this implies that there is no important difference in apparent activation energy between those reactions. However the partial pressure of hydrogen did affect the relative rates of olefinic and aromatic hydrodechlorination reactions at constant temperature. It was assumed that olefinic hydrodechlorination was of order n w.r.t. hydrogen, and aromatic hydrodechlorination was of order m w.r.t. hydrogen as described by the following equations.

$$d= \frac{k_{42}\ PH_2^{\,n}}{k_{42}\ PH^n + k_{43}\ PH^m}$$

$$a= \frac{k_{43}\ PH_2^{\,m}}{k_{42}\ PH_2^{\,n} + k_{43}PH_2^{\,m}}$$

therefore $$\frac{d}{a} = \left(\frac{k_{42}}{k_{43}}\right) PH_2^{\,n-m}$$

and $$\log \frac{d}{a} = \log \left(\frac{k_{42}}{k_{43}}\right) + (n-m) \log PH_2$$

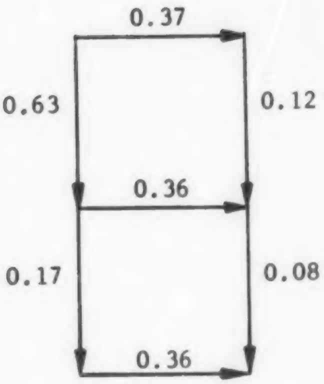
Fig. (3b-11) is a log-log plot of the ratio of olefinic aromatic relative rate constants ie. $\frac{d}{a}$, vs partial pressure of hydrogen at 200°C. The slope of the

DDE RELATIVE RATE CONSTANTS

.35% Pd on α-Al_2O_3

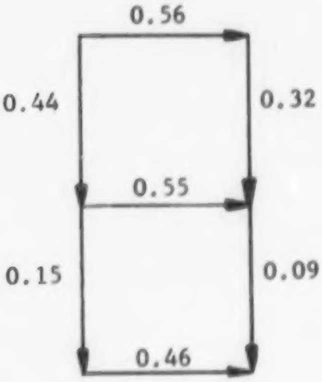
200°C

P_{H_2} = 60 mm Hg



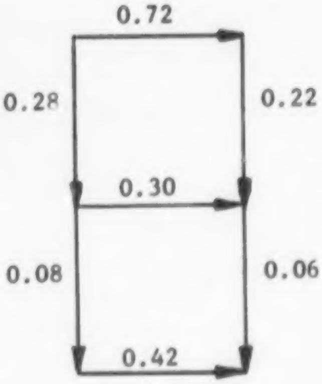
200°C

P_{H_2} = 140 mm Hg



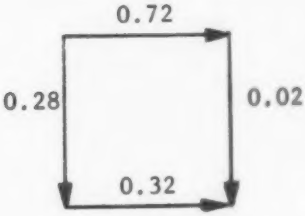
200°C

P_{H_2} = 580 mm Hg



170°C

P_{H_2} = 580 mm Hg



230°C

P_{H_2} = 580 mm Hg

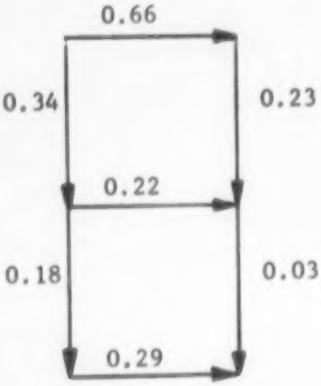
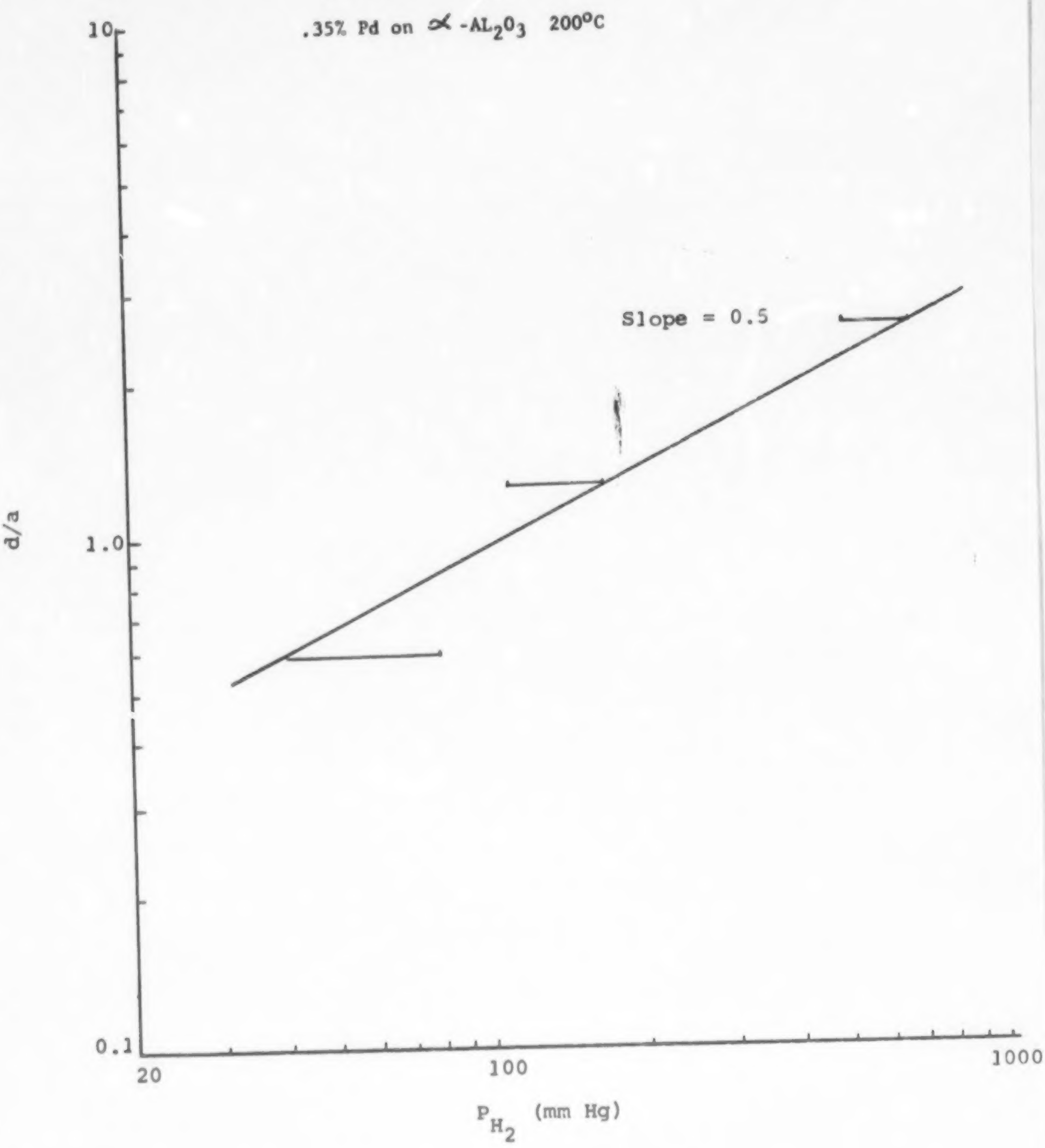


Figure (3B-11)

RATIO OF OLEFINIC TO AROMATIC DDE HYDRODECHLORINATION RATE CONSTANTS AS A FUNCTION OF H_2 PRESSURE



line (0.5) corresponded to the order difference in hydrogen between the olefinic aromatic reactions. Since the olefinic reaction has a higher order in hydrogen then that of the aromatic reaction, the relative rate constants of olefinic reactions decrease as PH_2 decreases. A Langmuir - Hinshelwood mechanism was assumed to describe the reaction system. The mechanism is based on dissociative adsorption of hydrogen and bimolecular surface reaction of DDE with H ie

$$-r_{DDE} = \frac{k\, K_{H_2}^{\frac{1}{2}}\, K_{DDE}\, PH_2^{\frac{1}{2}}\, P_{DDE}}{(1+K_{H_2}^{\frac{1}{2}}\, PH_2^{\frac{1}{2}} + K_{DDE}P_{DDE} + K\text{xylene } P\text{xylene})^2}$$

assuming that the KP terms are considerably greater than 1 gives

$$-r_{DDE} = \frac{kK_{H_2}^{\frac{1}{2}}\, K_{DDE}\, PH_2^{\frac{1}{2}}\, P_{DDE}}{(KH_2^{\frac{1}{2}}\, PH_2^{\frac{1}{2}} + K_{DDE}P_{DDE} + K\text{xylene } P\text{xylene})^2}$$

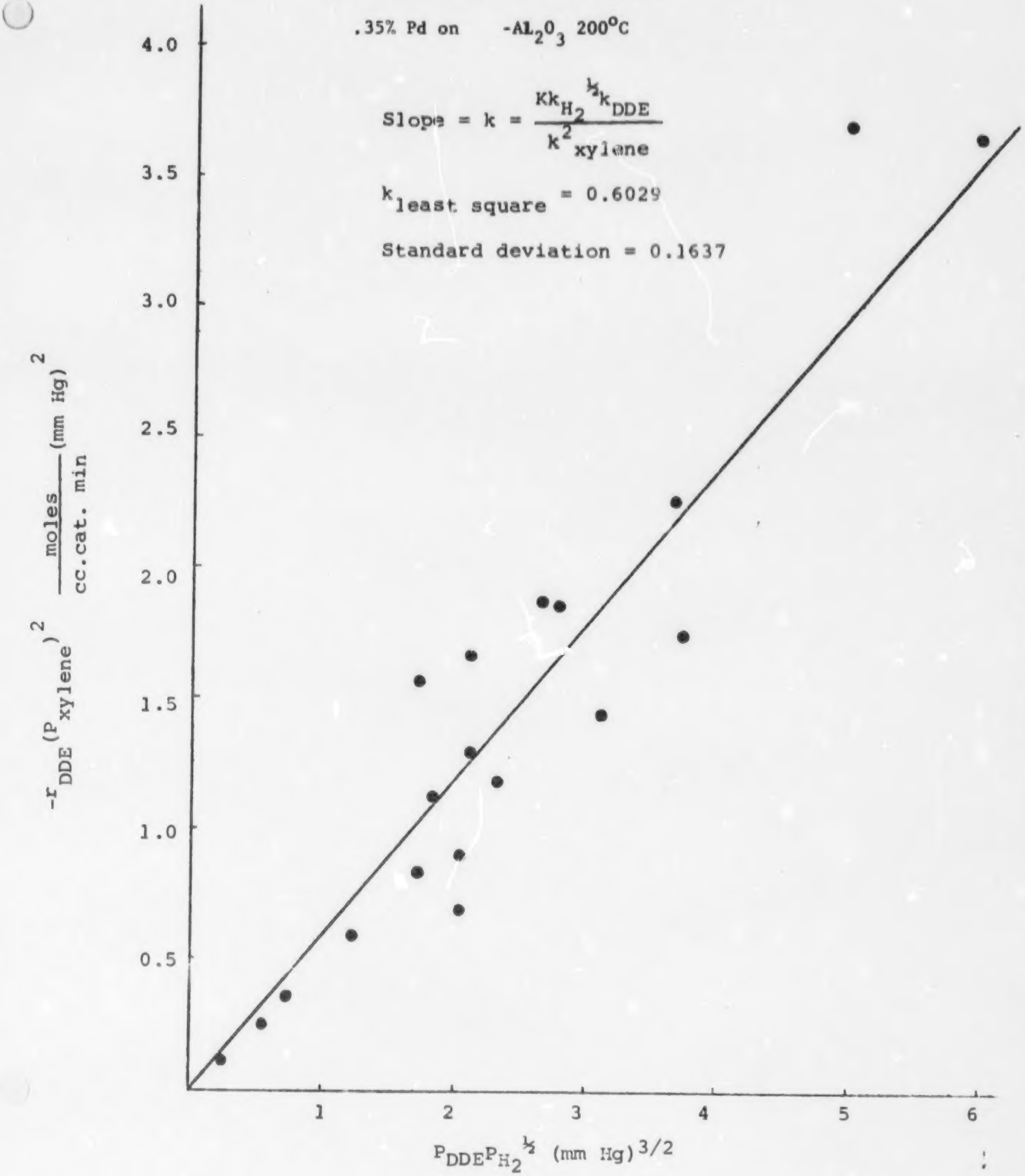
Under the reaction conditions studied. P_{DDE} is $\ll$ Pxylene and Pxylene $>$ $PH_2^{\frac{1}{2}}$ so that the $KH_2^{\frac{1}{2}}\, PH_2^{\frac{1}{2}}$ term is important only if $KH_2 > 5$ Kxylene. Therefore

$$(-r_{DDE})\, P^2\text{xylene} = \left(\frac{k\, KH_2^{\frac{1}{2}}\, K_{DDE}}{K^2\text{xylene}}\right) PH_2^{\frac{1}{2}}\, P_{DDE}$$

Fig. (3b-12) is a plot of $(-r_{DDE})\, P^2$xylene vs $PH_2^{\frac{1}{2}}\, P_{DDE}$ at 200°C. It was also found that if the catalyst was used at 170°C first and at 200°C later observed rates were lower than expected. This behavior may be the result of accumulation of less volatile species on the catalyst at lower temperatures. A least square fit of the data on figure (3b-12) gave a value of $\frac{kK_{H_2}^{\frac{1}{2}}\, K_{DDE}}{K^2\text{xylene}} = .60$ with a standard deviation of $\pm$, 16. Further Langmuir - Hinshelwood plots for olefinic and aromatic chlorine reactions of DDE were constructed by separating $(-r_{DDE})$ into $(-r_{DDE}$ olefinic) and $(-r_{DDE}$ aromatic) by the corresponding relative rate constants shown in Fig. (3b-10); the resulting plots are shown in Fig. (3b-13). It was found that $(-r_{DDE}$ olefinic) vs $PH_2\, P_{DDE}$ and $(-r_{DDE}$ aromatic) vs $PH_2^{\frac{1}{2}}\, P_{DDE}$ gave lower percentage deviation than the other ordinates tried.

Figure (3b-12)

DDE HYDRODECHLORINATION KINETICS



.35% Pd on $-Al_2O_3$ 200°C

$$\text{Slope} = k = \frac{Kk_{H_2}^{1/2}k_{DDE}}{k^2_{xylene}}$$

$k_{\text{least square}} = 0.6029$

Standard deviation = 0.1637

Figure (3b-13)

DDE AROMATIC AND OLEFINIC H_2 PRESSURE DEPENDENCE

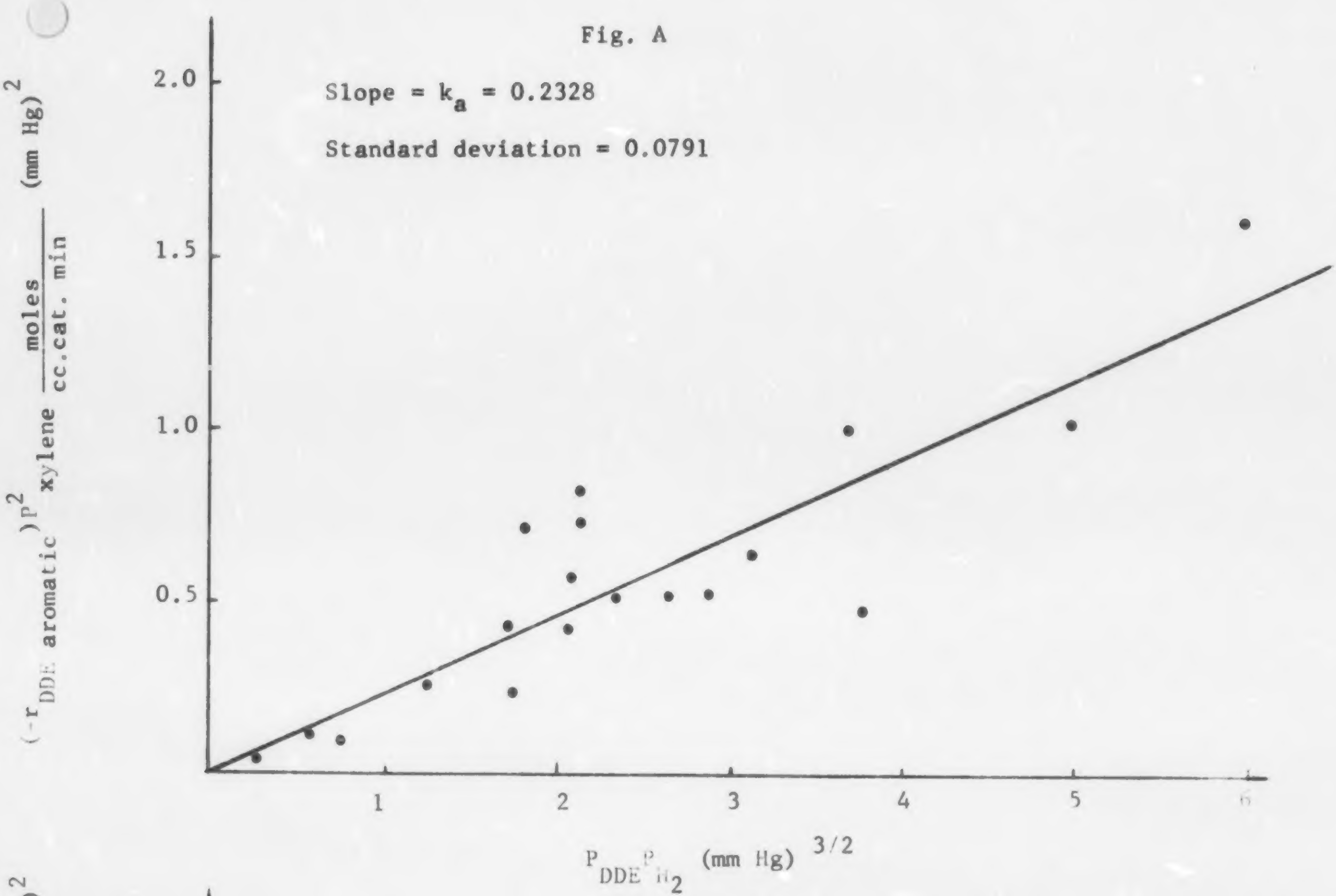


Fig. A

Slope = k_a = 0.2328

Standard deviation = 0.0791

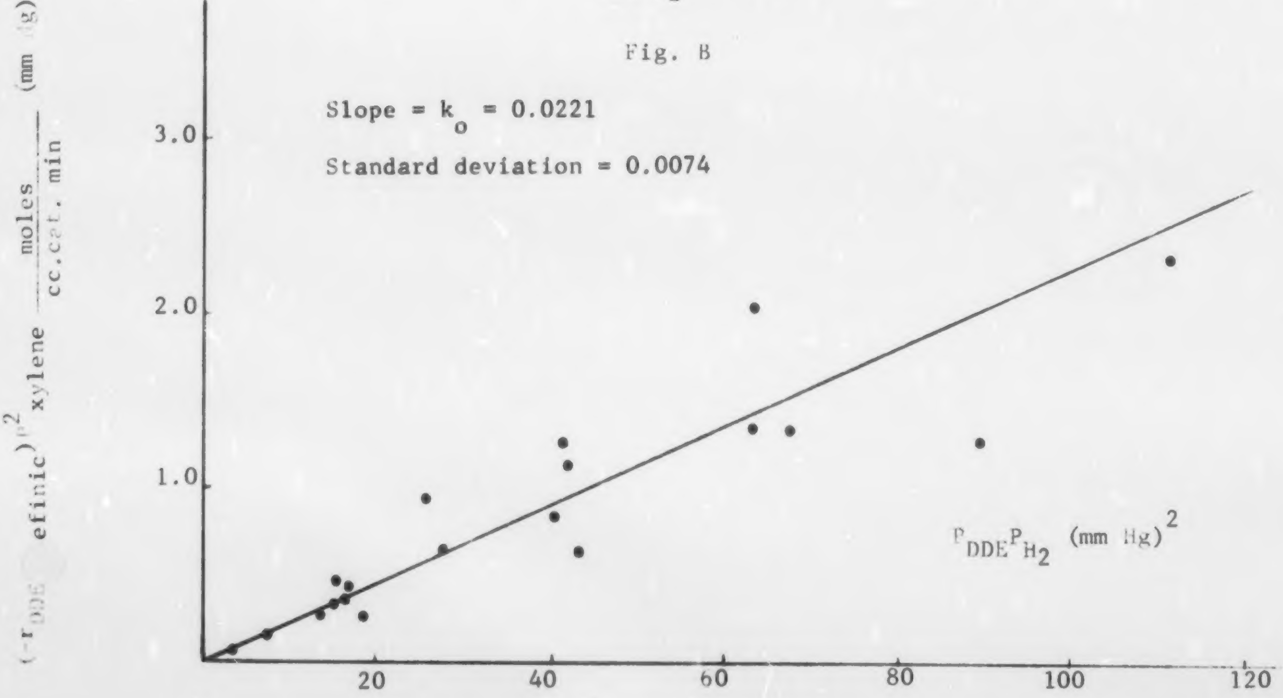


Fig. B

Slope = k_o = 0.0221

Standard deviation = 0.0074

LIQUID PHASE EXPERIMENTS

A series of preliminary experiments in the Teflon autoclave was made with DDT to determine if a hydrocarbon solvent, xylene, and an inexpensive acid acceptor ($Ca(OH)_2$) could be used in the liquid phase hydrodechlorination process with Ni catalyst. The results and the experimental conditions are summarized in Table (3b-3).

In general only a trace amount of the desired product, 1,1-diphenyl ethane was formed. Intermediate product distribution was complex. As in previous experiments, the effect of increasing hydrogen pressure from 3.4-25 atm. was negligible (compare Run DR4 to DR15). Increasing catalyst concentration by a factor of 5 shows that the conversion was not a linear function of catalyst loading (see DR1 and DR5).

The most successful experiments in this series occurred when the volume of solution was kept small and the probability for direct contact of insoluble $Ca(OH)_2$ and nickel catalyst was the highest (DR4, DR11, DR12). When xylene was substituted by ethanol (DR18), $Ca(OH)_2$ as acid acceptor appeared to be still much less effective than soluble NaOH (compare DR18 and DR20). The main conclusion derived from these studies is that it is preferable that the acid acceptor be soluble in the reaction medium, so that the nickel-catalyzed hydrodechlorination reaction can proceed at a reasonable rate with high selectivity to the desirable products. In addition, the use of a polar solvent may facilitate polarization of the C-Cl bond and thereby enhance catalytic activity.

Table (3b-3)

Experiments on DDT in Liquid Phase under Different Conditions

Run No	wt of DDT gm	Vol of Soln cc(x,1)	Amount of cat** gm	Temp ^{0}C	Pressure atm	Time hr	Cl_2 conv %*	Selectivity ***	Remark
DR-1	10	500	.0261	140	3.4	18	36.1	1 - 26% 4 - 57%	base $Ca(OH)_2$ DDT mixture contained 50% wettable ingredients
DR-4	10	100	.2517	140	3.4	18	68	1 - 42 2 - 58	"
DR-5	50	250	.2620	140	3.4	18	39	1 - 30 4 - 52	"
DR-6	100	195	2.00	140	3.4	18	39	1 - 26 2 - 10 4 - 60	The technical DDT was separated from the wettable mixture. Amount of DDT in soln. ≈40.0 gm ($Ca(OH)_2$) base
DR-7	100	175	see remark	140	3.4	18	27	1 - 17 2 - 2 4 - 80	amount of DDT in soln. ≈ 31 gm cat is as reused from DR-6.
DR-8	100	165	"	140	3.4	18	24	1 - 13 2 - 2 4 - 60	cat was reused from DR-7 amount of DDT in soln. ≈29 gm
DR-9	125	200	2.01	180	3.4	20	43	1 - 23 2 - 13 4 - 60	amount of DDT in soln ≈ 39 gm
DR-11	10	100	.2517	140	3.4	18	72	1 - 41 2 - 49	technical DDT
DR-12	10	75	.2327	140	3.4	18	70	1 - 41 2 - 53	amount of DDT in soln ≈ 4.6 gm
DR-13	10	200	1.00	140	25	50	47	1 - 20 2 - 37 4 - 45	analytical grade DDT was used $Ca(OH)_2$ base

Table (3b-3) (cont.)

Run No	wt of DDT gm	Vol of soln cc(xyl)	Amount of cat** gm	Temp °C	Pressure atm	Time hr	Cl_2 conv %*	Selectivity ***	Remark
DR-15	10	200	1.00	140	25	18	40	1 - 20 2 - 14 4 - 57	analytical grade DDT was used $Ca(OH)_2$
DR-16	5	100	.505	140	25	18	56	1 - 32 2 - 39 4 - 28	"
DR-18	10	10C	.5	140	25	18	50	1 - 32 2 - 39 4 - 28	Solvent was EtOH $Ca(OH)_2$
DR-20	5	100	.2520	140	25	18	69	1 - 40 2 - 48	Soln. EtOH(Na(OH))
DR-22	10	200	1.00	100	50	18	95	0 - 70 1 - 29	"

*Cl conversion is calculated as $\frac{[Cl]_o - [Cl]_t}{[Cl]_t}$ where $[Cl]_t = \sum_{i=1}^{i=x} i\, Cl_i$ and Cl_i is the percentage amount of products containing i atoms of chlorine

**catalyst Ni on kieselgahr

***first number is the chlorine number, the second is the percentage amount of product with chlorine number shown by the first figure

A further series of experiments was carried out in the Teflon autoclave to investigate

(1) liquid phase stoichiometry of both Ni and Pd catalyzed DDE hydrodechlorination

(2) reaction paths and associated relative rate constants

(3) catalyst loading and stirrer speed effects on reaction rate

(4) hydrogen pressure and temperature effects on rate and selectivity. Data obtained in the atmospheric pressure liquid phase reactor (experiment LS-4) are included to extend the data set. Table (3b-4) lists the experimental conditions for this set of experiments. In Experiments DDE (2-11R) the catalyst used was 10% Pd on charcoal and in DDE (12-15R) 61% Ni on Kieselguhr was employed. Data sets, including analytical data (see section 5-b for details), and computed reaction paths superimposed on selectivity plots for this series of experiments are found on pages (3-64, 3-88).

(1) Liquid Phase Stoichiometry.

Similar to the gas phase experiments, both Ni and Pd catalyzed liquid phase reactions showed concerted removal of both olefinic chlorines. DDD was not observed, indicating that olefinic hydrodechlorination is a precursor to olefinic hydrogenation.

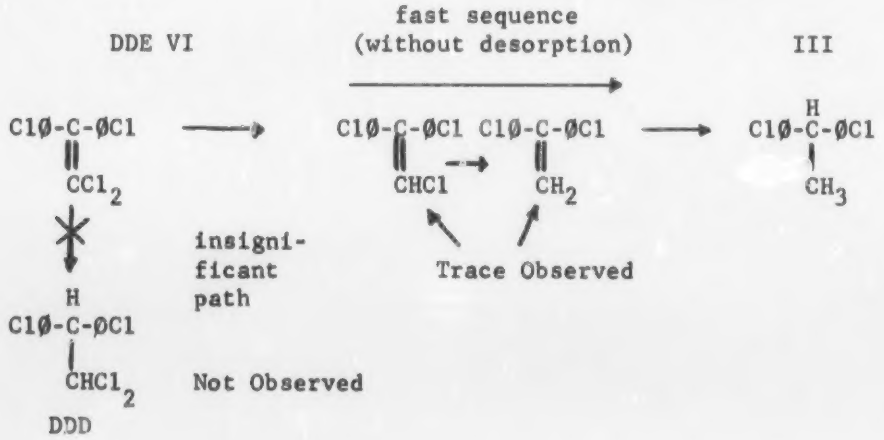


TABLE (3b-4)

Experimental Conditions for Batch DDE Kinetic Studies Conducted in Teflon Autoclave

99 gm ETOH, 1.0 gm DDE, .5526 gm NaOH

Exp. No.	Catalyst	Catalyst Wt. (mg.)	Activation Temp. °C	H_2 Pressure (bar)	Reaction Temp. (°C)	Stirrer Speed (RPM)
DDE 1	Pd Black	30.0	220	50	100	1500
DDE 2	10% Pd on C	30.0	↓	↓	|	↓
DDE 3	↓	10.0			|	
DDE 4		20.0			|	
DDE 5		30.0			60	
DDE 5R		↓			60±5	
DDE 5R△1					59.5±1.5	900
DDE 6					24-47	1500
DDE 7				5	22-42	↓
DDE 8				7	100±4	
DDE 9				20	24-47	
DDE 10				↓	98±2	
DDE 11				50	80.5±2.5	
DDE 11R				↓	81.5±2.5	

TABLE (3b-4) (cont.

Exp. No.	Catalyst	Catalyst Wt. (mg.)	Activation Temp. (°C)	H_2 Pressure (bar)	Reaction Temp. (°C)	Stirrer Speed (RPM)
DDE 12	61% Ni on K	50.0	220	50	99±1	1500
DDE 12R	↓	↓	370	↓	100±	↓
DDE 13	↓	↓	220	↓	81.5±3.5	↓
DDE 13R	↓	↓	370	↓	80±1	↓
DDE 14	↓	↓	220	↓	60.5±2.5	↓
DDE 14R	↓	↓	370	↓	60±3	↓
DDE 15	↓	↓	220	↓	27-42	↓
DDE 15R	↓	↓	370	↓	25-41	↓
LS-4*	10% Pd on C	62.1	220	1 atm	23	

* 1.008 gm. DDT, 100 cc Etoh, .7421 gm NaOH

DDE 2 ANALYTICAL RESULTS

reaction time (min)		5	10	15	25	35	45	60	90	120	165
sample #	0	1	2	3	4	5	6	7	8	9	10
R.T. *											
.283	.0022	.0151	.0339	.0583	.0667	.0877	.0998	.01475	.2295	.2682	.3449
.307											
.476											
.500											
.584											
.711	.0193	.2052	.2422	.3207	.3667	.3734	.3887	.4004	.3795	.3630	.3067
.717											
.789	.0081	.0118	.0167	.0163	.0144	.0142	.0093	.0084	.0046	.0033	.0020
.940	.0211	.0608	.0200	.0345	.0448	.0515	.1045	.0443	.0203	.0210	
1.000	.9373	.6514	.5153	.3897	.3104	.2437	.1867	.1196	.0382	.0237	.0179
1.072											
1.120											
1.187											

* Relative Retention Time to PP' DDE

DDE 3 ANALYTICAL RESULTS

reaction time (min)	5	15	40	70	85	115	195	460	1045
sample #	1	3	5	7	8	9	10	11	12
R.T. *									
.283	.0027	.0017	.0065	.0057	.0063	.0126	.0112	.0224	.0405
.307									
.476	.0023	.0112	.0307	.0250	.0280	.0402	.0451	.1179	.1494
.500	.0077			.0033	.0073	.0091	.0161		.0430
.584									
.711	.0369	.0770	.1710	.2423	.2694	.3205	.3977	.5414	.6676
.717									
.789	.0059	.0041	.0106	.0074	.0076	.0075	.0085	.0052	.0051
.940	.0150	.0153	.0175	.0246	.0223	.0232	.0246	.0220	.0096
1.000	.9294	.8906	.7636	.6893	.6554	.5868	.4968	.2889	.0843
1.072									
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 4 ANALYTICAL RESULTS

reaction time (min)	0	8	18	28	43	58	88	118	178	268
sample #	0	1	2	3	4	5	6	7	8	9
R.T. *										
.283	.0056	.0177	.0328	.0362	.0627	.0781	.1382	.1348	.1906	.2567
.307										
.476	.0193	.0592	.1108	.1102	.1913	.2130	.2983	.2539	.3144	.3478
.500				.0181				.0240		
.534									.0018	
.711					.3414	.3832	.3822	.4224	.3990	.3563
.717	.0529	.1840	.2585	.3164						
.789	.0093	.0116	.0148	.0130	.0141	.0127	.0111	.0076	.0062	.0019
.940	.0195	.0211	.0183	.0186	.0130	.0122	.0083	.0076	.0043	.0037
1.000	.8937	.7063	.5647	.4876	.3774	.3008	.1619	.1498	.0733	.0336
1.072										
1.120										
1.187										

* Relative Retention Time to PP' DDE

DDE 5 ANALYTICAL RESULTS

reaction time (min)	0	10	20	30	45	60	90	120	180	265
sample #	0	1	2	3	4	5	6	7	8	9
R.T. *										
.283	.0048	.0091	.0156	.0240	.0429	.0441	.0528	.0639	.0971	.1430
.307										
.476	.0124	.0517	.0880	.1364	.2180	.2156	.2319	.2630	.3027	.3536
.500										
.584										
.711	.0298			.3392	.4148	.4492	.5361	.5521	.5205	.4667
.717		.1905	.2757							
.789	.0115	.0113	.0128	.0147	.0158	.0129	.0083	.0072	.0041	.0017
.940	.0318	.0308	.0297	.0219	.0192	.0311	.0246	.0189	.0218	.0099
1.000	.9097	.7047	.5759	.4637	.2894	.2471	.1464	.0948	.0405	.0251
1.072										
1.120										
1.187										

* Relative Retention Time to PP' DDE

DDE 5R ANALYTICAL RESULTS

reaction time (min)		5	20	35	50	65	95	140	260
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283		.0023	.0054	.0259	.0142	.0086	.0137	.0168	.0250
.307									
.476	.0116	.0192	.0404	.1688	.0875	.0765	.1102	.1345	.1706
.500					.0085				
.584									
.711	.0373			.3182	.4078	.4569	.5346	.6203	.6840
.717		.1231	.2533						
.789	.0065	.0090	.0116	.0233	.0162	.0146	.0115	.0126	.0092
.940	.0128	.0243	.0234	.0062	.0142	.0369	.0235	.0172	.0063
1.000	.9270	.8138	.6619	.4559	.4490	.4042	.3016	.2231	.1016
1.072	.0048	.0078	.0040	.0017	.0026	.0023	.0049	.0019	.0034
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 5RΔ1 ANALYTICAL RESULTS

reaction time (min)		15	30	45	75	120	180	240
sample #	0	1	2	3	4	5	6	7
R.T. *								
.283	.0034	.0031	.0172	.0350	.0150	.0147	.0195	.0222
.307	.0013							
.476		.0176	.0906	.1749	.1235	.1211	.1536	.1724
.500			.0142					
.584								
.711		.1146	.2328	.2897	.4081	.5204	.6165	.6697
.717								
.789		.0079	.0257	.0315	.0122	.0123	.0101	.0090
.940		.0179	.0047	.0040	.0099	.0160	.0077	.0061
1.000	.9351	.8358	.6130	.4636	.4312	.3128	.1902	.1179
1.072			.0018	.0013		.0028	.0024	.0026
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 6 ANALYTICAL RESULTS

Reaction time (min)		280	500	1390	1750	2820
sample #	0	7	8	9	10	11
R.T. *						
.283		.0024	.0079	.0116	.0256	.0186
.307						
.476	.0051	.0042	.0290	.0202	.0388	.0415
.500						
.584						
.711	.0204	.0454	.0959	.2262	.3386	.0415
.717						
.789	.0042	.0055	.0138	.0056	.0047	.0069
.940	.0110	.0189	.0134	.0314	.0310	.0330
1.000	.9593	.9236	.8401	.7050	.5611	.4896
1.072						
1.120						
1.187						

* Relative Retention Time to PP' DDE

DDE 7 ANALYTICAL RESULTS

Reaction time (min)	0	240	480	1200	1395	1590
sample #	0	1	2	3	4	5
R.T. *						
.283	.0016	.0950	.2146	.5239	.5897	.6411
.307						
.476	.0063	.2748	.4128	.3553	.3336	.3028
.500						
.584						
.711	.0217	.3543	.3531	.0995	.0767	.0561
.717						
.789	.0066	.0160	.0011			
.940	.0196	.0113	.0018	.0022		
1.000	.9443	.2485	.0166	.0191		
1.072						
1.120						
1.187						

* Relative Retention Time to PP' DDE

DDE 8 ANALYTICAL RESULTS

Reaction time (min)		15	40	50	60	90	120	145	925
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283	.0196	.0291	.0591	.0872	.1128	.1443	.1942	.2335	.4876
.307				.0014	.0017	.0015			
.476	.0226	.0800	.1480	.2152	.2565	.3024	.3608	.3918	.3540
.500	.0026	.0119	.0180	.0217	.0204	.0184	.0113		
.584					.0016	.0017	.0016	.0015	
.711				.2472	.2736	.2840	.2818	.2734	.1186
.717	.0564	.1706	.2388						
.789	.0149	.0241	.0269	.0314	.0323	.0289	.0253	.0206	.0038
.940	.0300	.0343	.0471	.0460	.0202	.0174	.0082	.0061	
1.000	.8527	.6506	.4621	.3498	.2810	.2013	.1168	.0732	.0360
1.072									
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 9 ANALYTICAL RESULTS

Reaction time (min)	0	15	45	75	180	240	360	1530
sample #	0	1	2	3	5	6	7	8
R.T. *								
.283			.0015	.0018	.0038	.0041	.0077	.0365
.307								
.476		.0080	.0113	.0138	.0253	.0349	.0593	.1983
.500								
.584								
.711		.0235	.0383	.0515	.1057	.1375	.2064	.5164
.717								
.789	.0026	.0060	.0058	.0062	.0021	.0082	.0115	.0180
.940								
1.000	.9974	.9484	.9308	.9018	.8580	.8042	.7151	.2307
1.072								
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 10 ANALYTICAL RESULTS

Reaction time (min)	0	5	15	30	45	75	105	225	405
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283	.0040	.0133	.0322	.0610	.0848	.1275	.1561	.2843	.4165
.307									
.476	.0134	.0603	.1379	.2268	.2917	.3740	.4006	.4421	.4078
.500	.0019	.0145	.0296	.0315	.0122				
.584									
.711				.3984	.4255	.4135	.3958	.2542	.1553
.717	.0524	.1949	.3363						
.789	.0082	.0152	.0204	.0200	.0127	.0122	.0044	.0030	
.940	.0130	.0164	.0127	.0100	.0045				
1.000	.8996	.6853	.4291	.2509	.1686	.0727	.0432	.0148	.0263
1.072	.0076		.0017	.0013				.0017	
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 11 ANALYTICAL RESULTS

Reaction time (min)	0	15	30	60	90	150	210	270	367	1166
sample #	0	1	2	3	4	5	6	7	8	9
R.T. *										
.283		.0036	.0032	.0062	.0078	.0111	.0256	.0146	.0186	.0415
.307										
.476	.0048	.0214	.0251	.0472	.0643	.0907	.1668	.1347	.1559	.2669
.500	.0018	.0028	.0014	.0030	.0043	.0054	.0120	.0026		
.584	.0010	.0029				.0037		.0014		.0029
.711	.0209	.1331	.1904	.2828	.3511	.4478	.4908	.5528	.6075	.6560
.717										
.789	.0049	.0065	.0118	.0103	.0152	.0145	.0178	.0184	.0152	.0055
.940	.0062	.0126	.0160	.0203	.0202	.0171	.0043	.0096	.0103	
1.000	.9549	.8144	.7475	.6276	.5347	.4080	.2827	.2646	.1887	.0250
1.072	.0056	.0027	.0045	.0025	.0023	.0017		.0012	.0038	.0023
1.120										
1.187										

* Relative Retention Time to PP' DDE

DDE 11 R ANALYTICAL RESULTS

Reaction time (min)	0	15	45	75	135	195	255	360	435
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283	.0115	.0344	.0892	.0798	.0987	.0706	.0845	.0535	.0612
.307									
.476	.0479	.2218	.4071	.3636	.3849	.3355	.3586	.2954	.3124
.500	.0091								
.584									
.711		.2547	.4205	.4944	.5035	.5856	.5569	.6420	.6153
.717	.0740								
.789	.0173	.0224	.0073	.0046					
.940	.0075	.0036							
1.000	.8255	.4623	.0760	.0577	.0128	.0083		.0091	.0110
1.072	.0072								
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 12 ANALYTICAL RESULTS

Reaction time (min)		15	30	45	60	127	180	240	315	1140
sample #	0	1	2	3	4	5	6	7	8	9
R.T. *										
.283	.0021	.0027	.0049	.0084	.0135	.0322	.0508	.0633	.0698	.1355
.307	.0019	.0028	.0021	.0041	.0036	.0048	.0053	.0011	.0005	
.476	.0029	.0053	.0216	.0537	.1032	.2500	.3501	.4099	.4159	.4905
.500	.0016	.0022	.0104	.0228	.0369	.0454	.0278			
.584	.0053	.0034	.0046							
.711	.0275	.0407	.1029	.1873	.2966	.4531	.4904	.4915	.4799	.3515
.717		.0100	.0400	.0500	.0300					
.798	.0067	.0074	.0121	.0169	.0194	.0167	.0100	.0030	.0012	
.940	.0129	.0153	.0137	.0123	.0108	.0083	.0052	.0034		
1.000	.9184	.8874	.7750	.6215	.4650	.1759	.0442	.0110	.0132	.0040
1.072	.0199	.0219	.0121	.0209	.0205	.0129	.0163	.0168	.0160	.0106
1.120										
1.187										

* Relative Retention Time to PP' DDE

DDE 14 ANALYTICAL RESULTS

Reaction time (min)		25	85	145	205	265	415	1165
sample #	0	1	2	3	4	5	6	7
R.T. *								
.283				.0044	.0100	.0173	.0338	.0778
.307								
.476	.0061		.0014	.0428	.1194	.1978	.3694	.5028
.500				.0136	.0309	.0305		
.584								
.711	.0141		.0368	.1429	.2529	.3242	.4396	.4109
.717								
.789			.0038	.0114	.0206	.0230	.0266	
.940	.0061	.0058	.0071	.0065	.0050	.0051		
1.000	.9598	.9810	.9366	.7779	.5593	.3990	.1306	.0084
1.072	.0139	.0129	.0109		.0018	.0016		
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 13 ANALYTICAL RESULTS

Reaction time (min)		22	52	82	142	202	262	1102
sample #	0	1	2	3	4	5	6	7
R.T. *								
.283	.0040	.0048	.0027	.0025	.0037	.0039	.0050	.0211
.307								
.476	.0136	.0224	.0066	.0038	.0090	.0191	.0331	.2259
.500								
.584								
.711	.0170	.0253	.0230	.0443	.1179	.2334	.3387	.7065
.717								
.789	.0026	.0021	.0031	.0041	.0078	.0129	.0155	.0030
.940	.0095	.0085	.0089	.0117	.0110	.0084	.0074	
1.000	.9445	.9224	.9428	.9191	.8395	.7049	.5800	.0354
1.072	.0083	.0145	.0126	.0141	.0111	.0101	.0057	.0080
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 15 ANALYTICAL RESULTS

Reaction time (hrs:min)	5	6	9	20:55	23:15	25	26:40	29:10
sample #	5	6	7	8	9	10	11	12
R.T. *								
.283			.0004	.0086	.0112	.0124	.0138	.0155
.307								
.476		.0055	.0188	.1225	.1462	.1820	.1923	.2069
.500			.0004	.0199	.0177			
.711				.4360	.4982	.5322	.5431	.5817
.719	.0291	.0517	.0235					
.789	.0027	.0041	.0072	.0215	.0243	.0247	.0340	.0311
.940	.0068	.0074	.0302	.0051	.0049	.0049	.0044	.0032
1.000	.9615	.9214	.8011	.3830	.2894	.2365	.2124	.1616
1.072		.0100	.0182	.0029	.0082	.0074		
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 12 R ANALYTICAL RESULTS

Reaction time (min)		5	15	30	60	120	180	240	300
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283	.0055	.0063	.0116	.0649	.1695	.1555	.3182	.3607	.4023
.307				.0090					
.476	.0147	.0176	.0685	.4053	.6326	.6193	.5912	.5664	.5349
.500			.0355	.0683					
.584									
.711	.0288	.0441	.0967	.1956	.1587	.1118	.0821	.0627	.0533
.717			.0300						
.789	.0037	.0048	.0174	.0266	.0044				
.940	.0067	.0078	.0075	.0038					
1.000	.9293	.9072	.7330	.2232	.0347	.0134	.0084	.0102	.0089
1.072	.0111	.0122		.0032					
1.120									
1.187									

* Relative Retention Time to PP' DDE

DDE 13 R ANALYTICAL RESULTS

Reaction time (min)		15	45	105	170	238	305	368
sample #	0	1	2	3	4	5	6	7
R.T. *								
.283				.0274	.1027	.1610	.1897	.2237
.307				.0022				
.476	.0103	.0144	.0089	.2352	.5704	.6267	.6242	.6250
.500				.0574				
.584								
.711	.0225	.0462	.0137	.1775	.2529	.2026	.1777	.1514
.717				.0400				
.789	.0013	.0018	.0026	.0261	.0157			
.940	.0070	.0100	.0067	.0053				
1.000	.9472	.9183	.9478	.4290	.0583	.0097	.0084	
1.072	.0117	.0094	.0112					
1.120								
1.187								

* Relative Retention Time to PP' DDE

DDE 14 R ANALYTICAL RESULTS

Reaction time (min)	167	262	322	414	572	1228
sample #	4	5	6	7	8	9
R.T. *						
.283		.0510	.0831	.1250	.1804	.4473
.307						
.476		.3950	.5079	.5873	.6042	.5058
.500						
.584						
.711		.2865	.3134	.2793	.2154	.0469
.717						
.789		.0390	.0310	.0083		
.940						
1.000		.2286	.0645			
1.072						
1.120						
1.187						

* Relative Retention Time to PP' DDE

DDE 15 R ANALYTICAL RESULTS

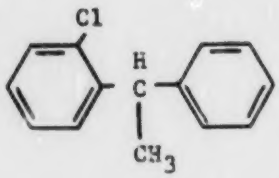
Reaction Time (min)		150	285	355	400	460	520	580	1410
sample #	0	1	2	3	4	5	6	7	8
R.T. *									
.283			.0300	.0528	.0590	.0878	.0990	.1227	.3895
.307									
.476		.0815	.3085	.4274	.4706	.550	.5734	.6021	.5460
.500									
.584									
.711		.0979	.2168	.2546	.2669	.2732	.2623	.2393	.0645
.717									
.789		.0223	.0422	.0383	.0398	.0320	.0308	.0039	
.940									
1.000	1.0000	.7982	.4024	.2268	.1636	.0589	.0344	.0320	
1.072		.0354	.0248	.0196	.0178	.0142	.0133	.0122	.0068
1.120									
1.187									

* Relative Retention Time to PP' DDE

LS-4 ANALYTICAL RESULTS

Reaction time (min)	10	54	127	307	542	1257	1927	2122
sample #	1	2	3	4	5	6	7	8
R.T. *								
.283			.014	.033	.050	.082	.102	.128
.307								
.446**				.006	.010	.025	.035	.046
.476		.052	.121	.221	.317	.430	.481	.517
.500								
.681***				.011	.012	.017	.019	.022
.711		.057	.093	.151	.195	.251	.255	.238
.717		SBS	SBS	SBS	SBS	SBS	SBS	SBS
.789	.006	.010	.016	.022	.022	.014	.006	.002
.940	.152	.144	.138	.121	.108	.084	.066	.048
1.000	.819	.715	.596	.421	.275	.097	.036	
1.072								
1.120								
1.187								

**



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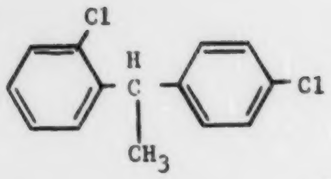
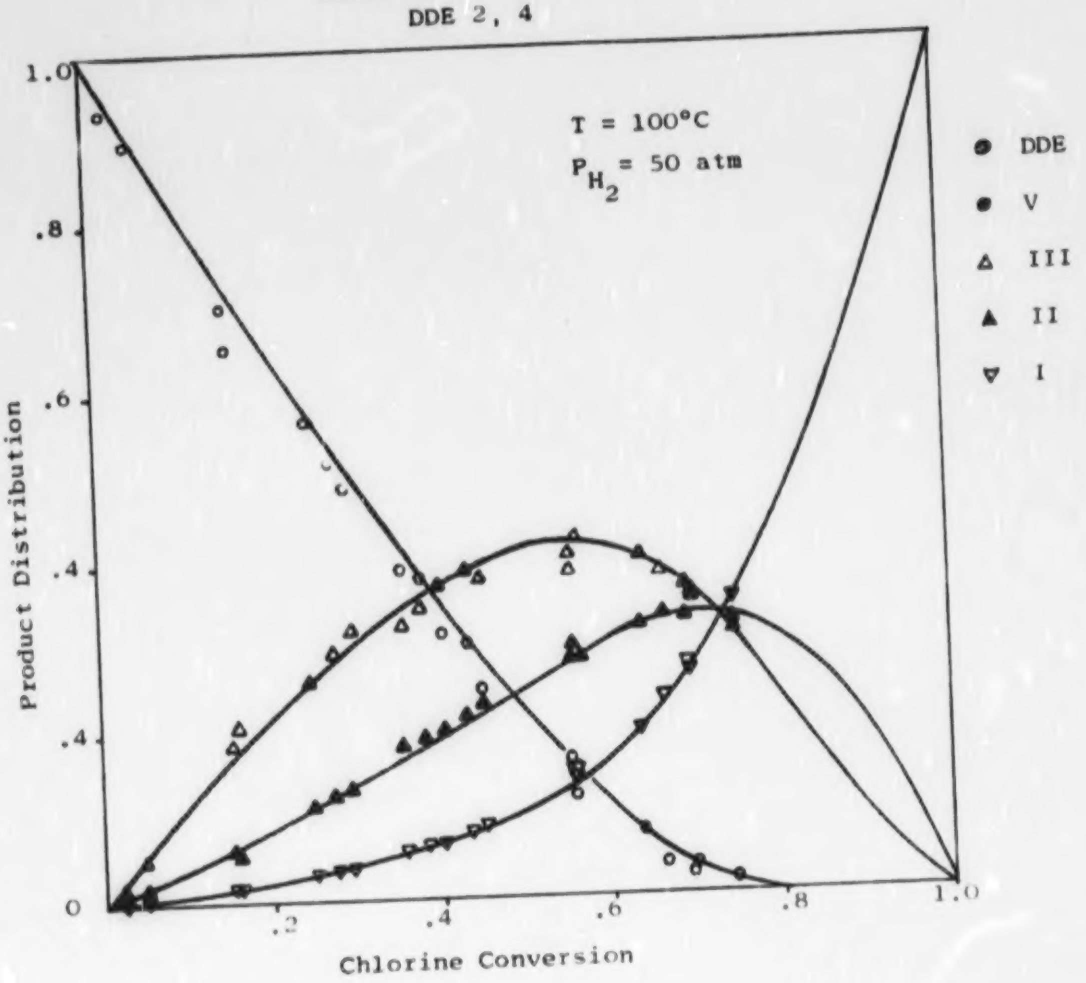
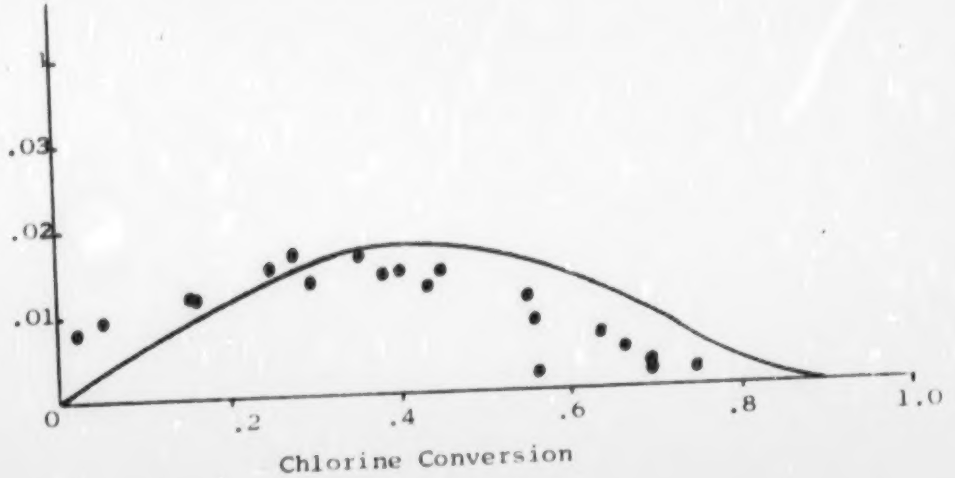


SELECTIVITY PLOT
DDE 2, 4





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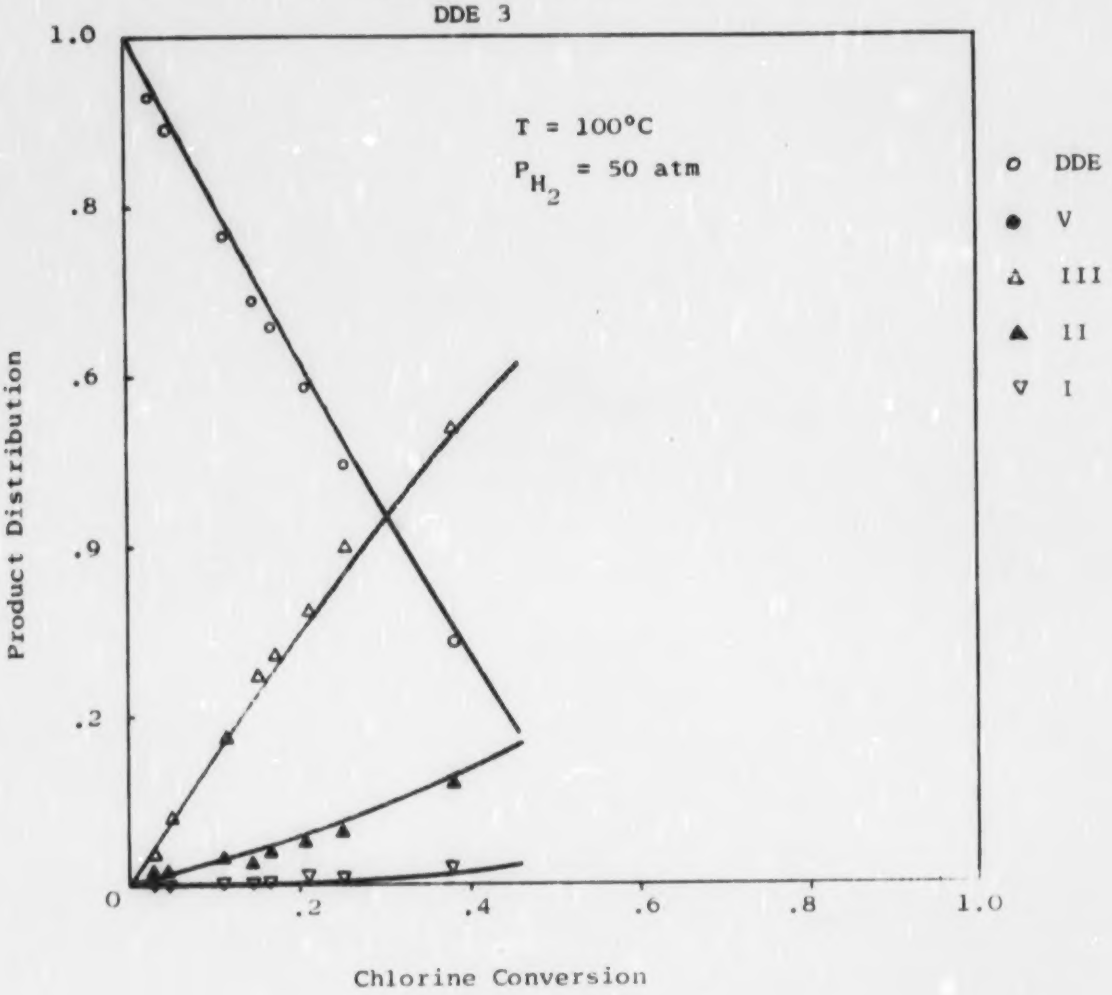

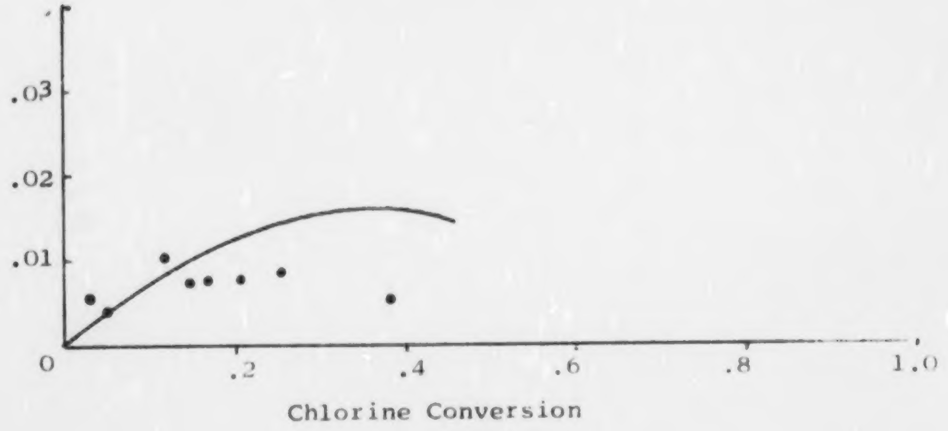

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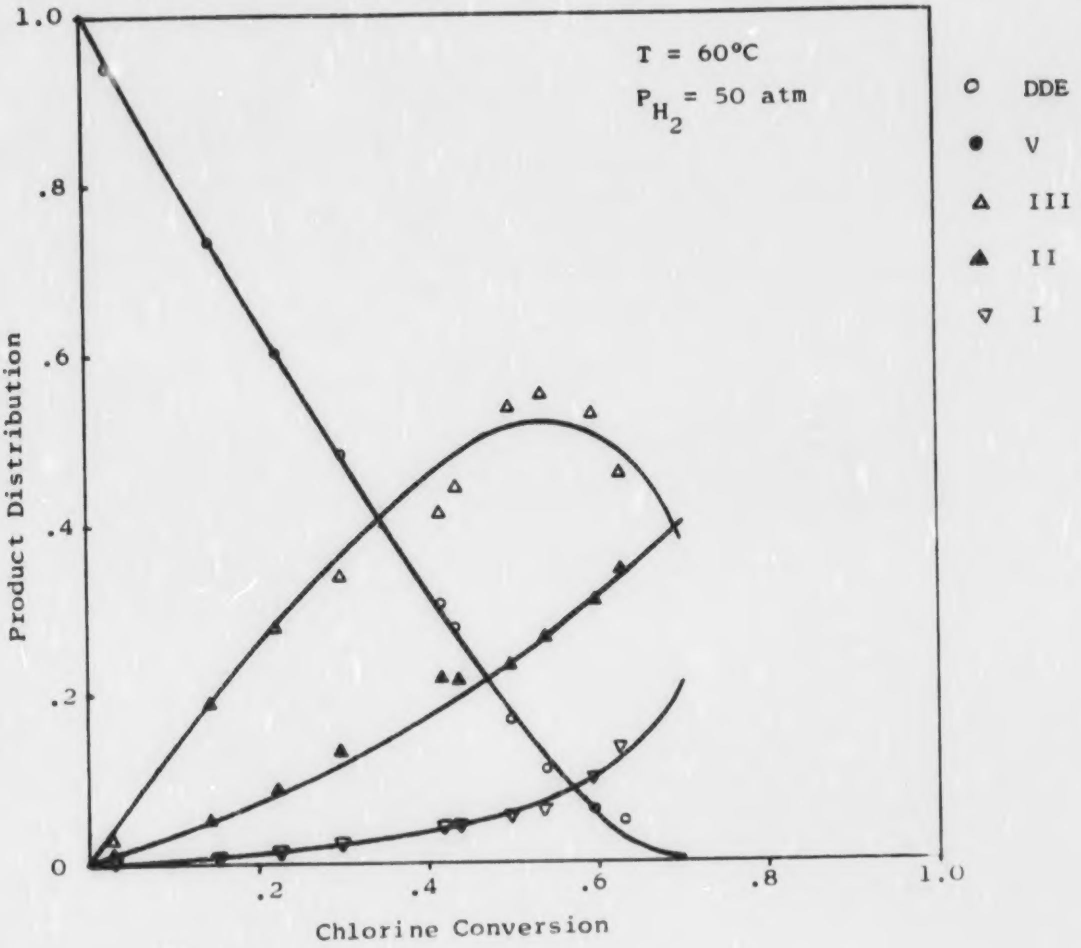
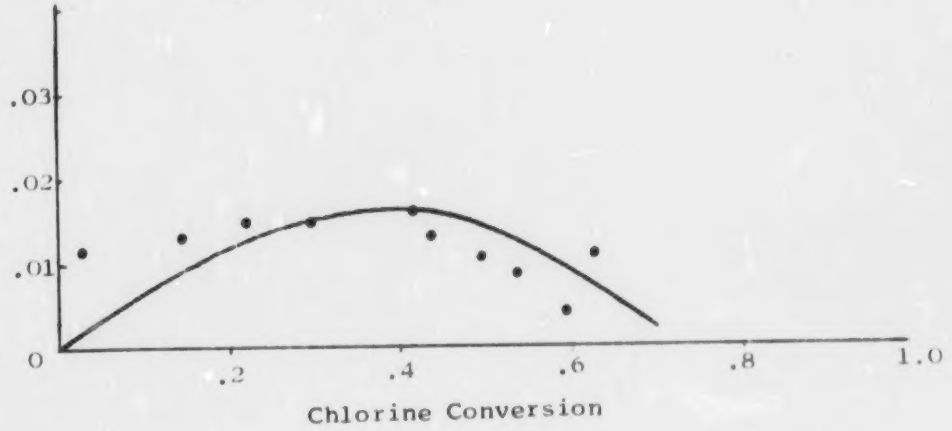
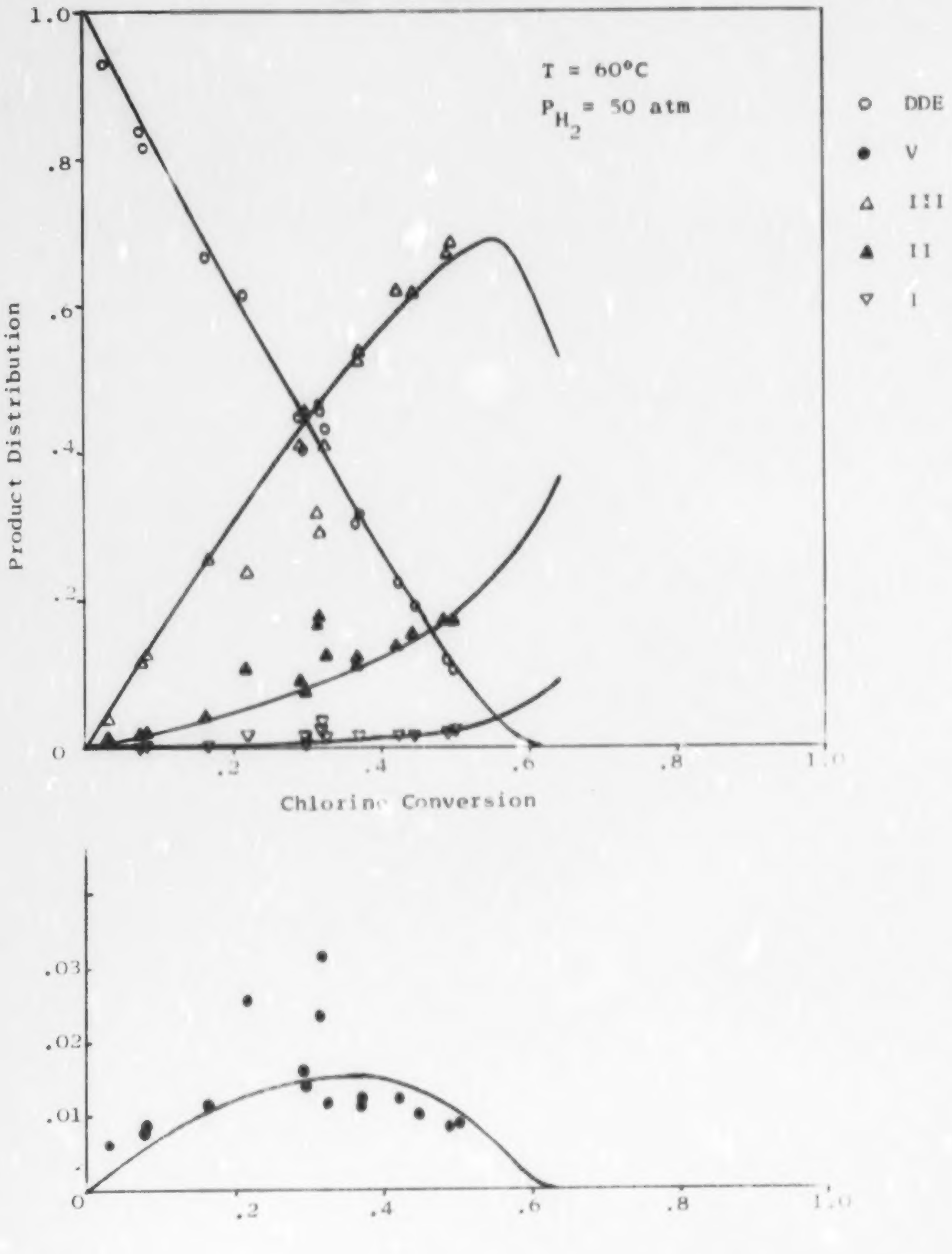
DDE 5





SELECTIVITY PLOT

DDE 5R, 5RΔ1



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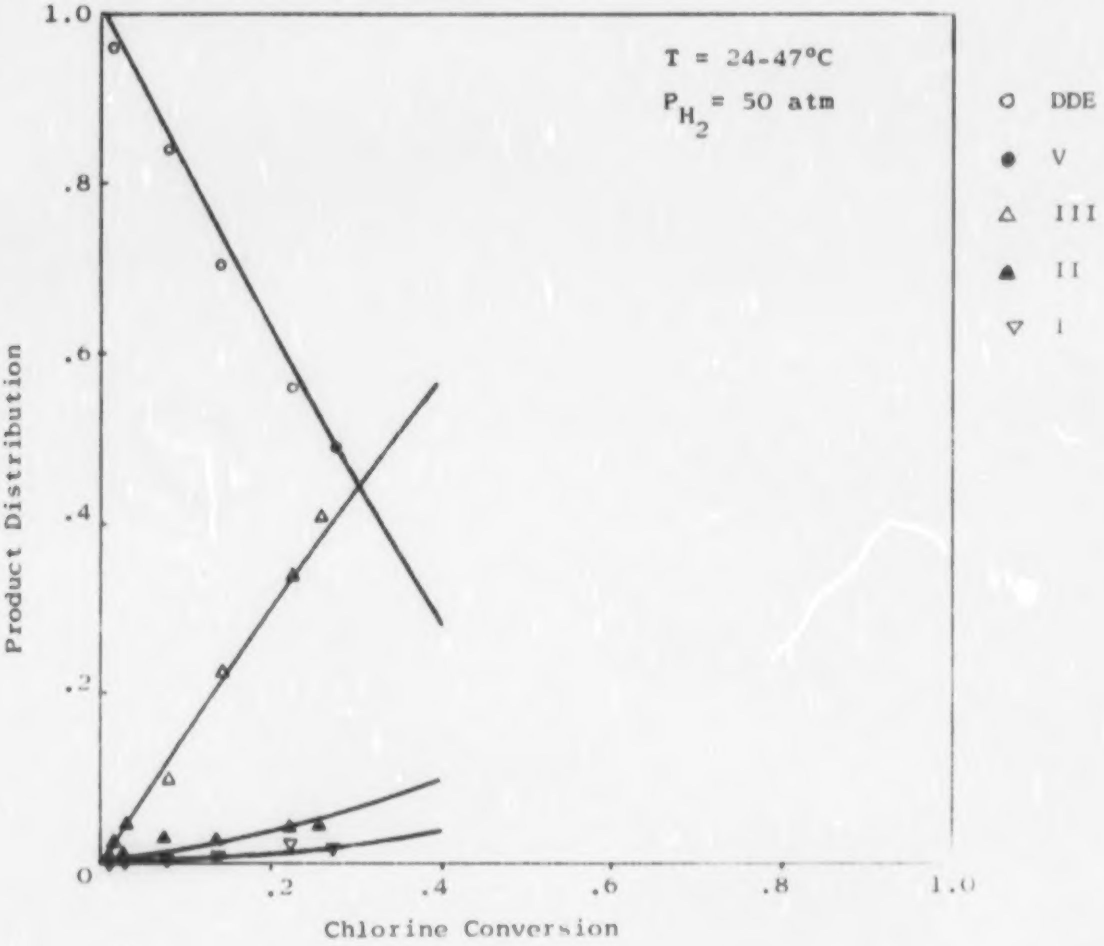
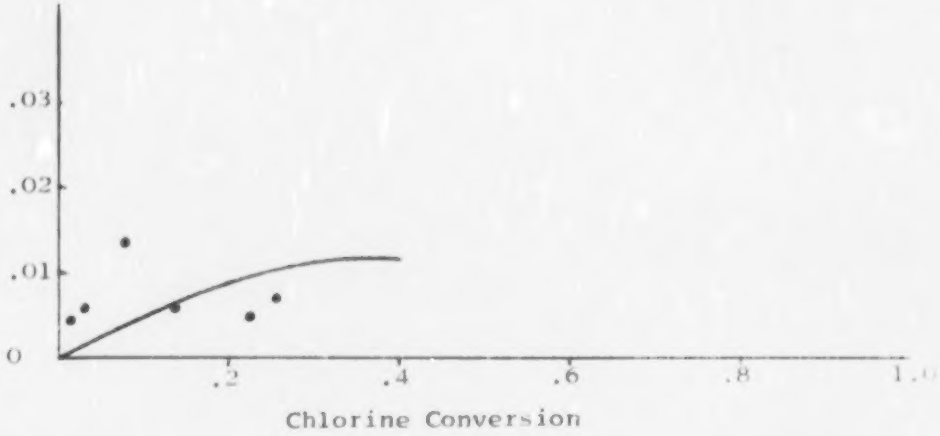
DDE 6





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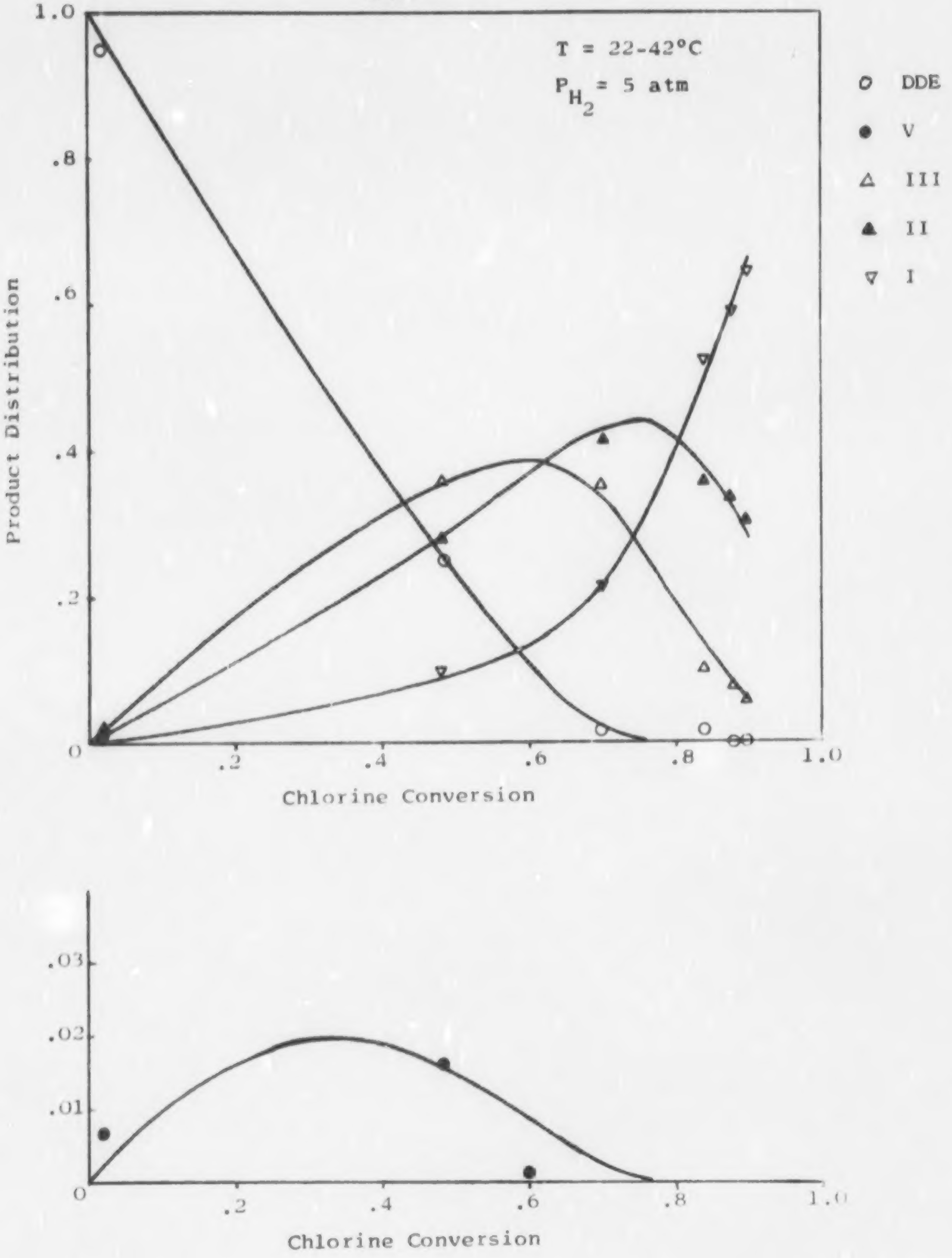
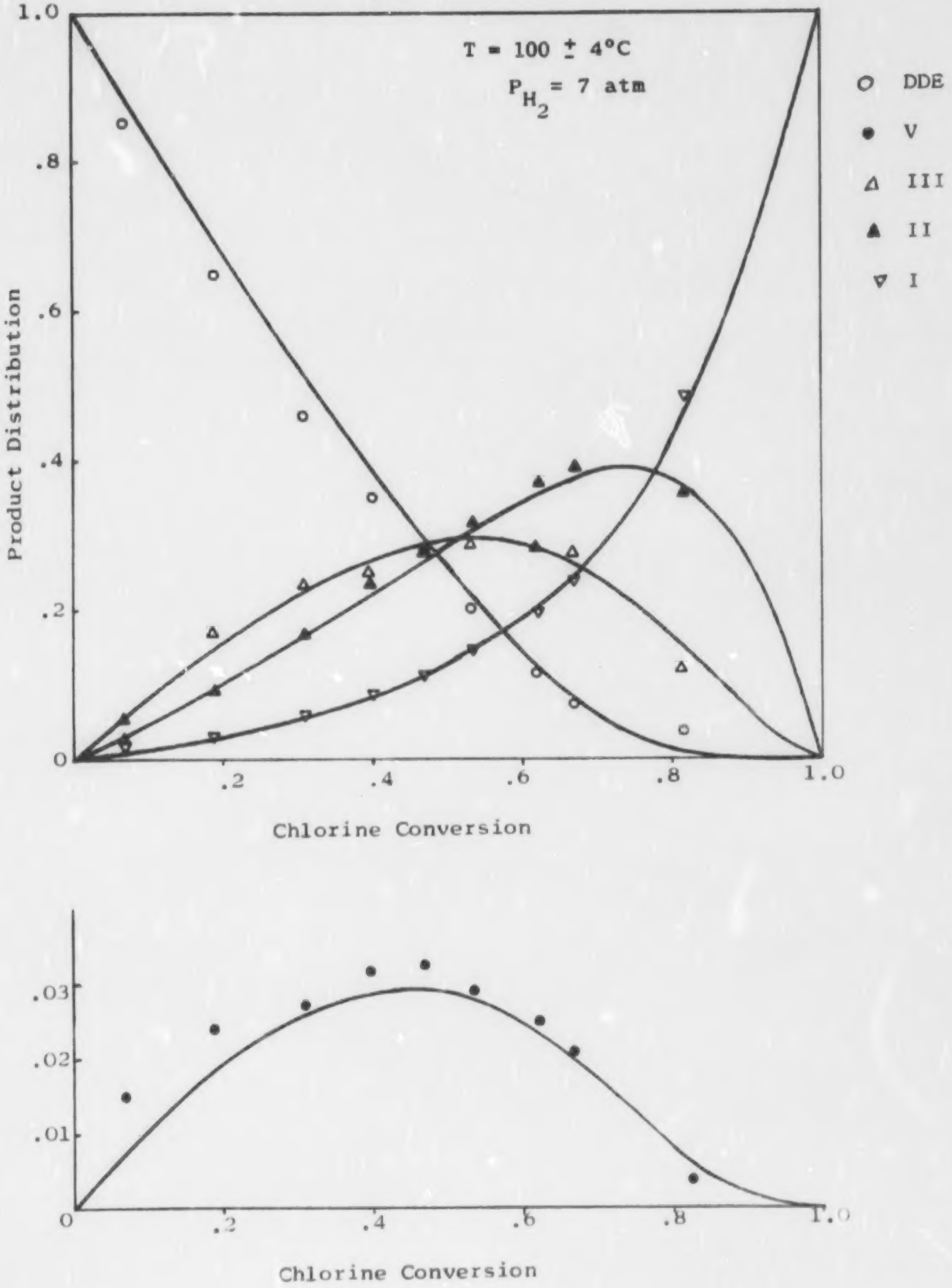
DDE 7



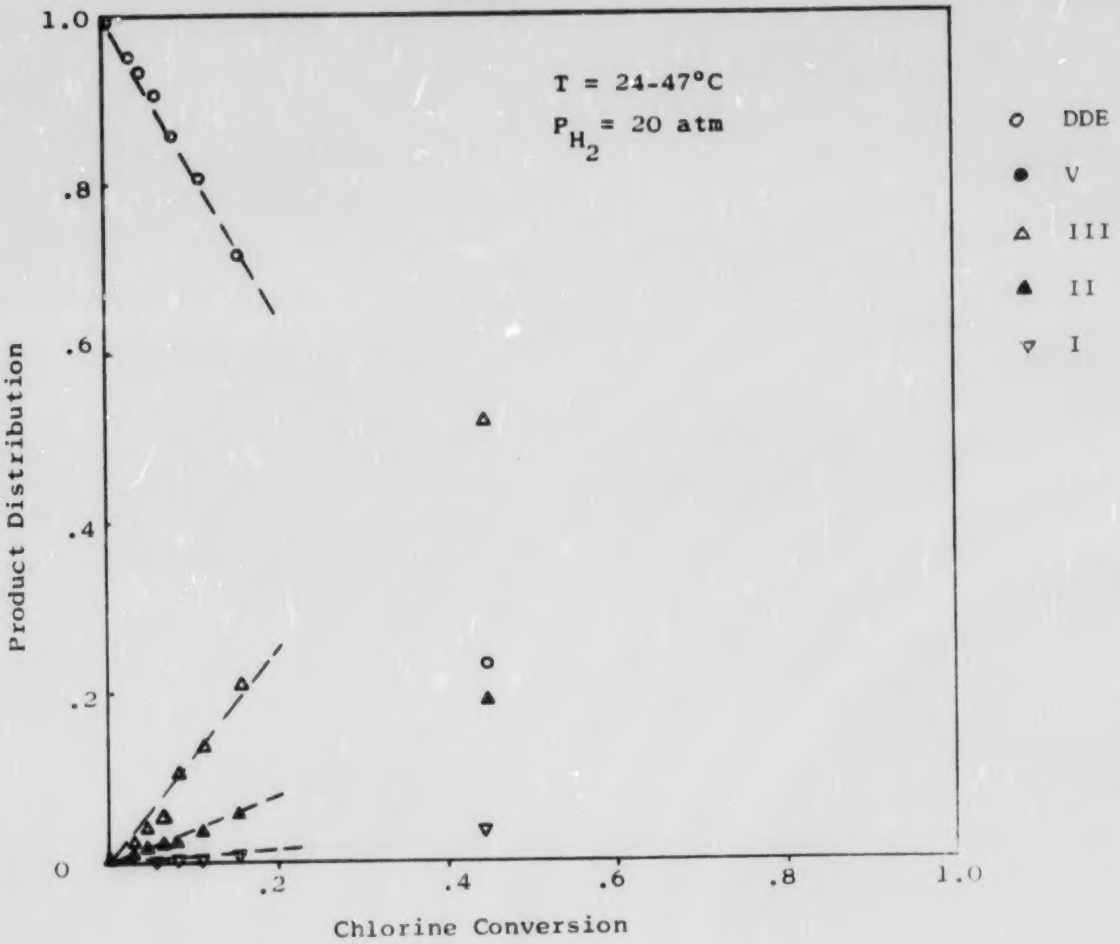
SELECTIVITY PLOT

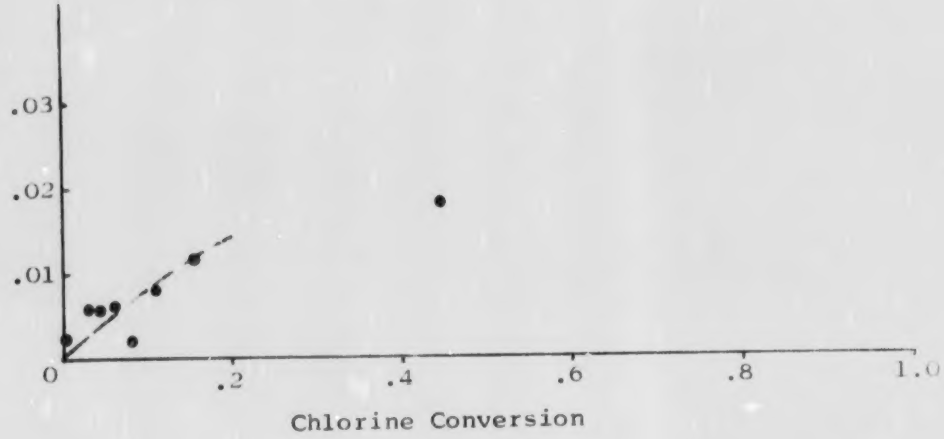
DDE 8



SELECTIVITY PLOT

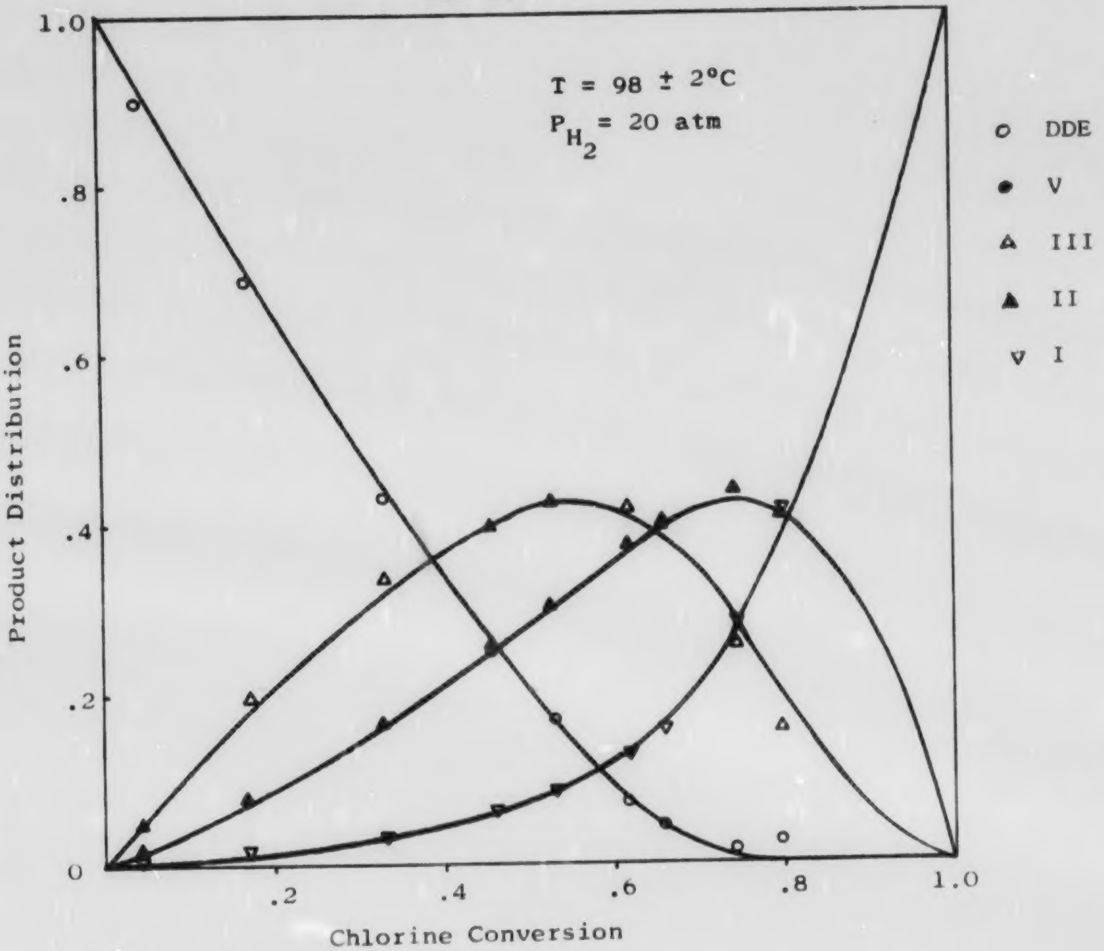
DDE 9

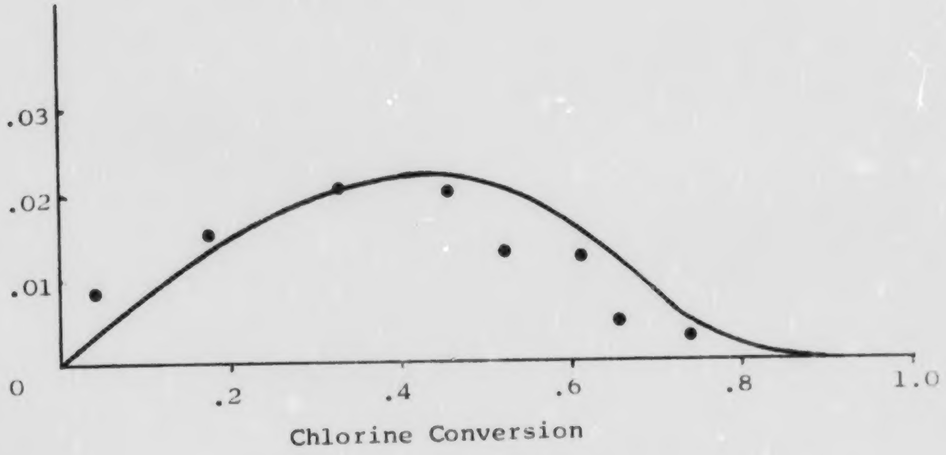




SELECTIVITY PLOT

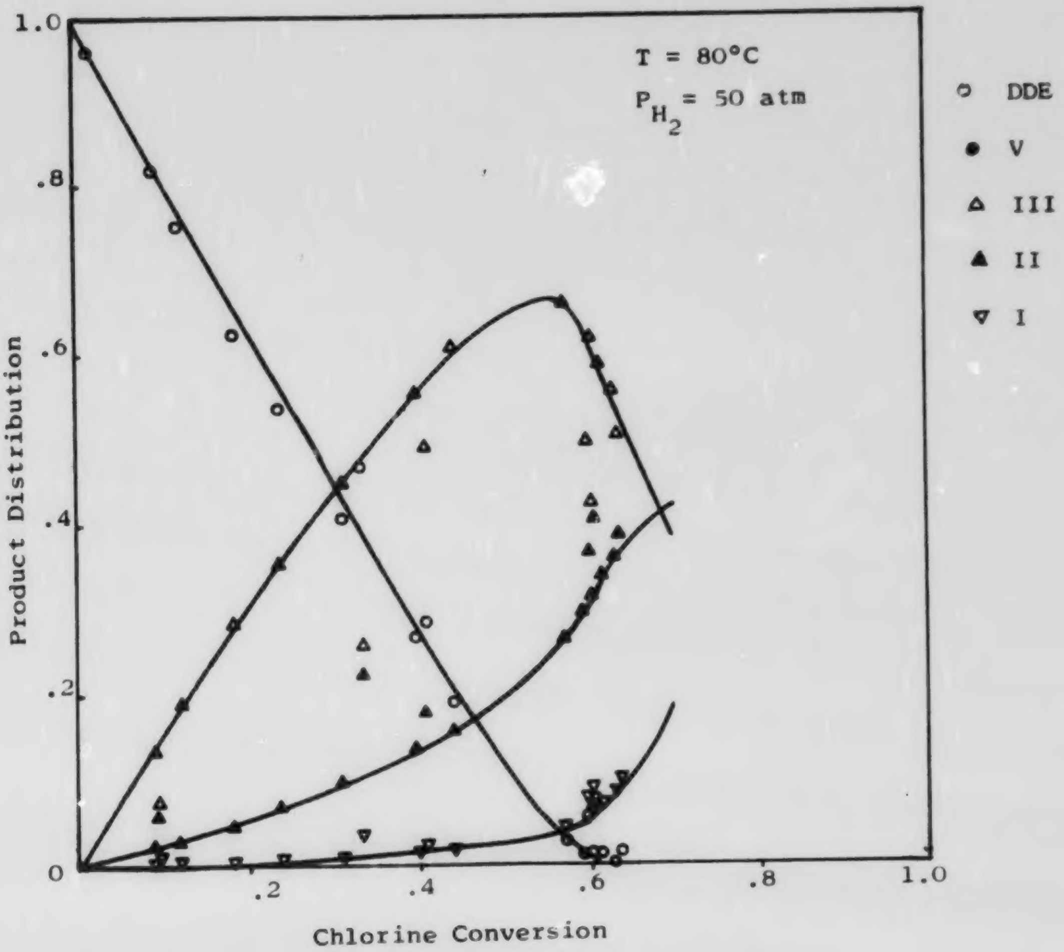
DDE 10





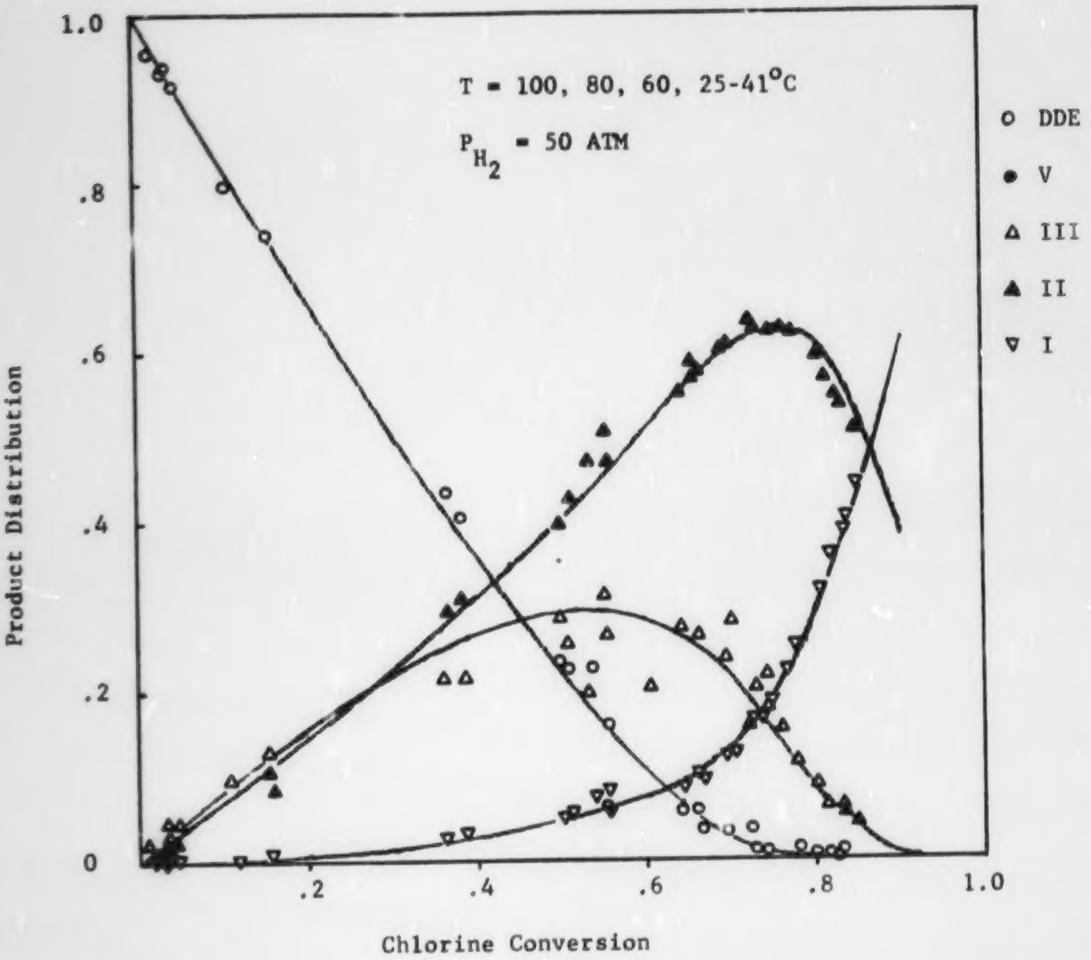
SELECTIVITY PLOT

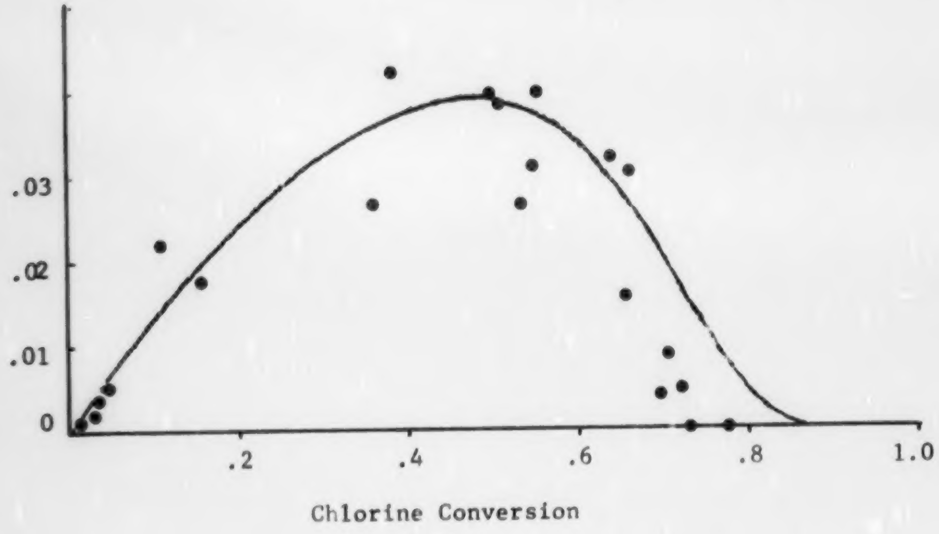
DDE 11, 11R



SELECTIVITY PLOT

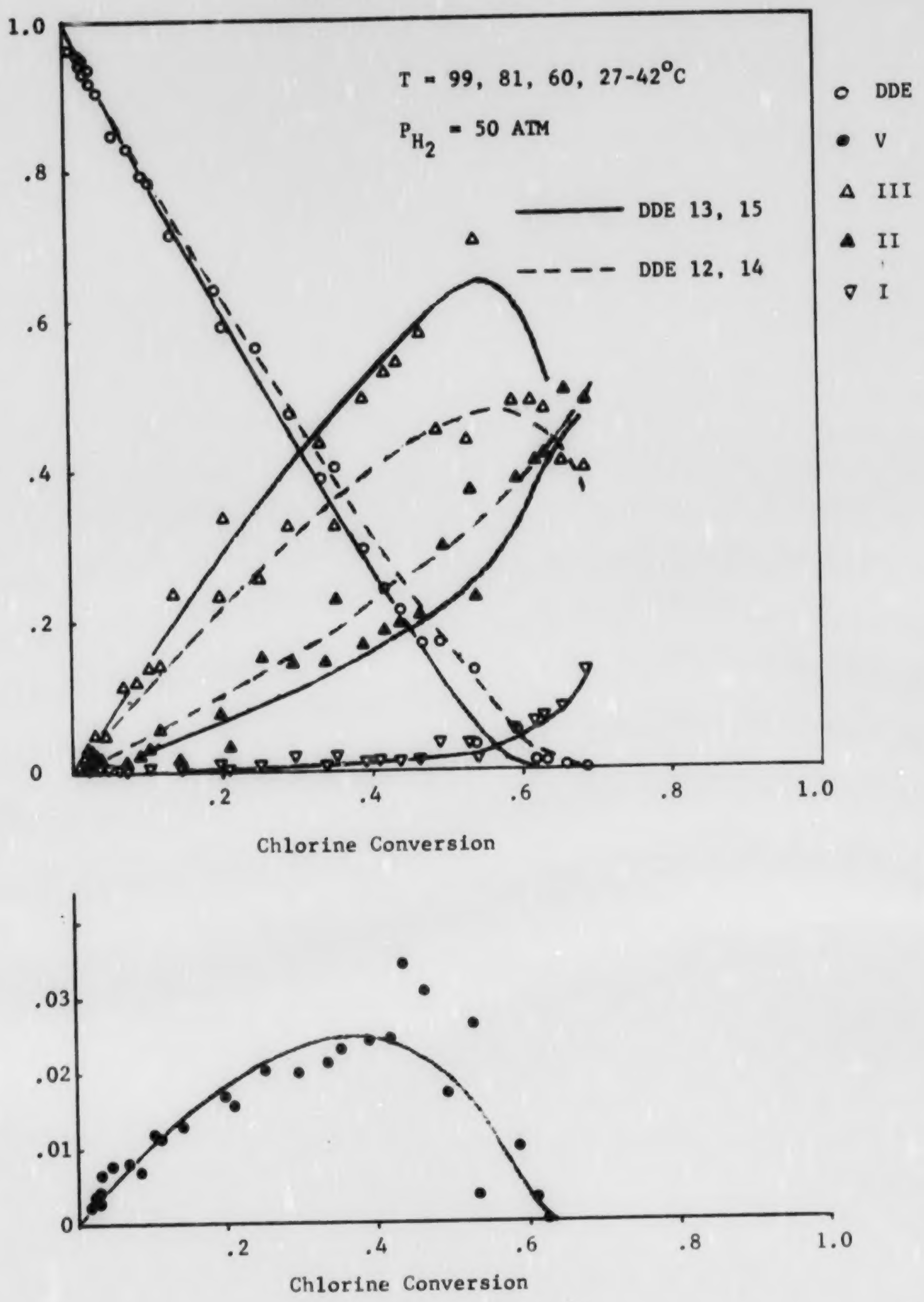
DDE 12R, 13R, 14R, 15R





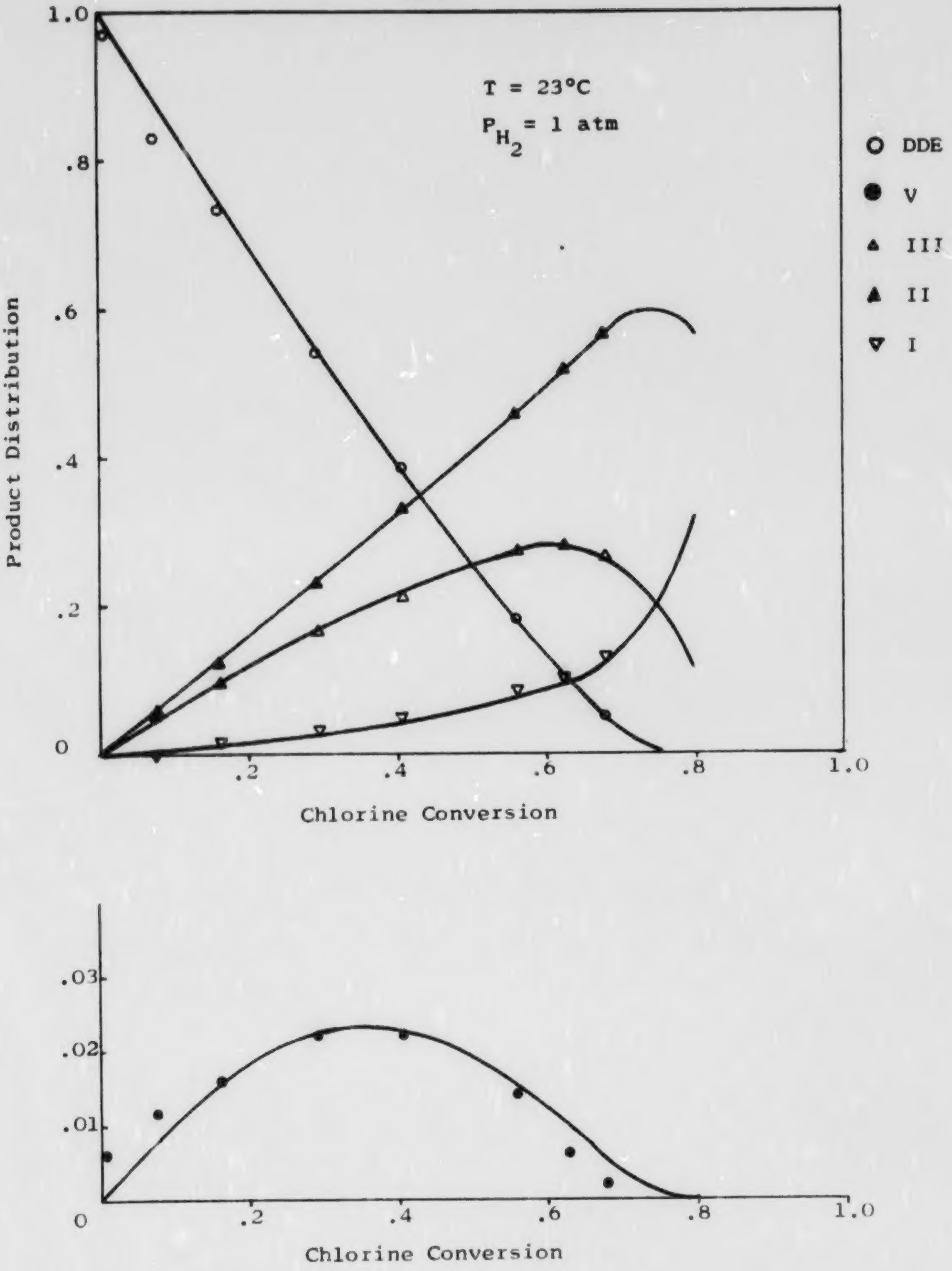
SELECTIVITY PLOT

DDE 12, 13, 14, 15,

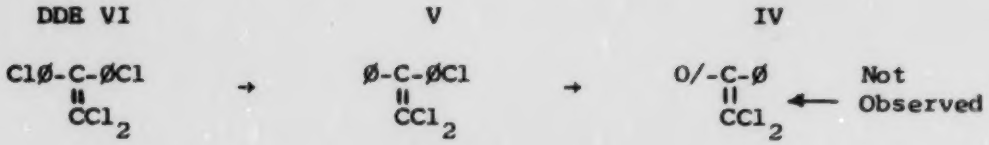


SELECTIVITY PLOT

LS-4

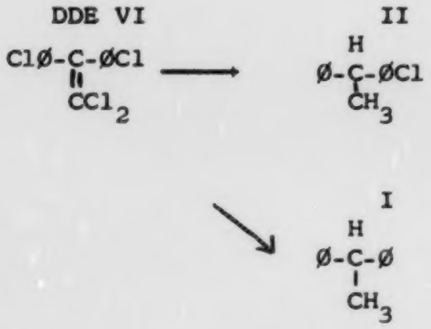


The parallel aromatic hydrodechlorination reactions of DDE



occurred to a much smaller extent than in the gas phase. The maximum amount of species V produced was typically 2-3 mole %. Further reaction of species V was characterized by loss of olefinic chlorine, while undetectable amounts of species IV were formed under these conditions.

However, the major difference between gas and liquid phase hydrodechlorination of DDE was the concerted or simultaneous removal of aromatic and olefinic chlorines.



Therefore, the overall stoichiometry for liquid phase hydrodechlorination of DDE is characterized as

$$\begin{tikzcd}
VI \arrow[r, "k_{63}"] \arrow[d, "k_{65}"'] \arrow[dr, "k_{62}"] \arrow[ddr, "k_{61}"] & III \arrow[d, "k_{32}"] \\
V \arrow[r, "k_{52}"] \arrow[d, "k_{54}"'] & II \arrow[d, "k_{21}"] \\
IV \arrow[r, "k_{41}"] & I
\end{tikzcd}$$

(2) Reaction paths

Similar to the treatment described for Aroclor 1248, DDE hydrodechlorination stoichiometry can be described by a set of normalized first order differential equations which simulate batch reaction behavior.

$$\frac{d\ V}{d\ VI} = \frac{k_{65}\ VI - (k_{52} + k_{54})\ V}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI}$$

$$\frac{d\ IV}{d\ VI} = \frac{k_{54}\ V - k_{41}\ IV}{-(k_{65} - k_{63} + k_{62} + k_{61})\ VI}$$

$$\frac{d\ III}{d\ VI} = \frac{k_{63}\ VI - k_{32}\ III}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI}$$

$$\frac{d\ II}{d\ VI} = \frac{k_{62}\ VI + k_{32}\ III - k_{21}\ II}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI}$$

$$\frac{d\ I}{d\ VI} = \frac{k_{61}\ VI + k_{21}\ II + k_{41}\ IV}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI}$$

There is no unique solution to this set of equations. However, simplifying assumptions can be applied to yield unique solutions.

At low DDE conversion

$$\frac{d\ V}{d\ VI} \approx \frac{k_{65}\ VI}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI} = \frac{\Delta V}{\Delta VI}$$

$$\frac{d\ III}{d\ VI} \approx \frac{k_{63}\ VI}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI} = \frac{\Delta III}{\Delta VI}$$

$$\frac{d\ II}{d\ VI} \approx \frac{k_{62}\ VI}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI} = \frac{\Delta II}{\Delta VI}$$

and

$$\frac{d\ I}{d\ VI} \approx \frac{k_{61}\ VI}{-(k_{65} + k_{63} + k_{62} + k_{61})\ VI} = \frac{\Delta I}{\Delta VI}$$

in this way k_{65}, k_{63}, k_{62}, and k_{61} (normalized to $(k_{65} + k_{63} + k_{62} + k_{61})$ may be determined from initial selectivity data.

The experimentally observed maximum selectivity values for reaction intermediates V*, IV*, III*, and II* where $\frac{d\ V}{d\ VI}$, $\frac{d\ IV}{d\ VI}$, $\frac{d\ III}{d\ VI}$, and $\frac{d\ II}{d\ VI}$ are respectively identically equal to zero give

$$(k_{52} + k_{54}) = \frac{k_{65}\ VI}{V^*}$$

$$k_{41} = \frac{k_{54}\ V}{IV^*}$$

$$k_{32} = \frac{k_{63}\ VI}{III^*}$$

and

$$k_{21} = \frac{k_{62}\ VI + k_{32}\ III}{II^*}$$

since species IV was produced in undetectable amounts, the following assumptions were made.

a. $k_{54} = 0.5\ k_{65}$

b. $k_{41} = k_{52}$

The simulated results were consistent with this approach in that only trace amounts of species IV were computed to exist during reaction. Table (3b-5) lists the values of the relative rate constants we have determined for these experiments. With these values, it is possible to determine the total initial olefinic and aromatic hydrodechlorination rate constants considering the number of chlorine atoms removed in any one step

$$k_{olefinic} = 2\ k_{63} + 2\ k_{62} + 2\ k_{61}$$

$$k_{aromatic} = k_{65} + k_{62} + 2k_{61}$$

Table (3b-6) lists $k_{olefinic}$, $k_{aromatic}$ and the ratio ka/(ka+ko) for these experiments.

Figure (3b-14) shows the dependence of the relative rate of aromatic to olefinic hydrodechlorination as a function of hydrogen pressure for the Pd catalyzed runs. As in the gas phase studies the olefinic hydrodechlorination rate is more pressure dependent than the aromatic rate.

TABLE (3b-5)

LIQUID PHASE DDE RELATIVE RATE CONSTANTS

Pd Catalyzed

	k_{65}	k_{63}	k_{62}	k_{61}	k_{52}	k_{32}	k_{21}
DDE 3	.04	.80	.14	.02		No Data	
DDE 2,4	.04	.65	.25	.06	.65	.23	.26
DDE 5	.04	.75	.17	.04	.75	.17	.13
DDE 5R,5RΔ1	.04	.82	.12	.02	.82	.06*	.04**
DDE 6	.03	.83	.09	.05		No Data	
DDE 7	.07	.54	.30	.09	1.6	.15	.10
DDE 8	.07	.53	.30	.10	.72	.38	.27
DDE 9	.05	.69	.22	.04		No Data	
DDE 10	.05	.64	.26	.05	.64	.20	.14
DDE 11,11R	.04	.80	.14	.02	.80	.06	.04
LS-4	.08	.38	.48	.06	1.53	.14	.05
		Ni Catalyzed					
DDE 12-15R	.08	.50	.40	.02	.50	.31	.08
DDE 12,14	.06	.64	.27	.03	.64	.12	.05
DDE 13,15	.06	.76	.17	.01	.76	.05	.025

* Estimated Value III* not experimentally observed

** Estimated Value II* not experimentally observed

TABLE (3b-6)

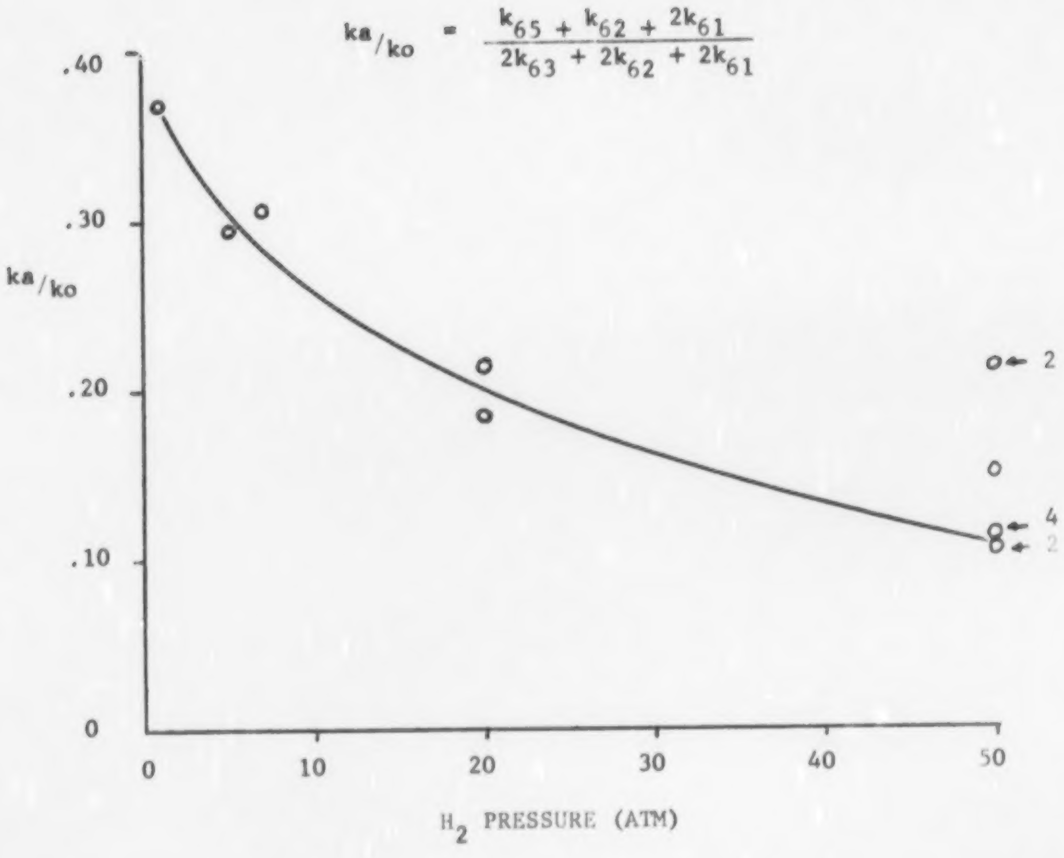
INITIAL RELATIVE RATES OF OLEFINIC AND AROMATIC DDE HYDRODECHLORINATION

	Initial Olefinic Rate $2\ k_{63} + 2\ k_{62} + 2\ k_{61}$	Initial Aromatic Rate $k_{65} + k_{62} + 2\ k_{61}$	$\frac{\text{Aromatic Rate}}{\text{Total Rate}}$
	Pd Catalyzed Experiments		
DDE 3	1.92	0.22	.103
DDE 2 + 4	1.92	0.41	.176
DDE 5	1.92	0.29	.131
DDE 5R 5RA1	1.92	0.20	.094
DDE 6	1.94	0.22	.102
DDE 7	1.86	0.55	.228
DDE 8	1.86	0.57	.236
DDE 9	1.90	0.35	.156
DDE 10	1.90	0.41	.177
DDE 11-11R	1.92	0.22	.103
LS-4	1.84	0.68	.270
	Ni Catalyzed Experiments		
DDE 12-15R	1.84	0.52	.22
DDE 12,14	1.88	0.39	.17
DDE 13,15	1.88	0.25	.12

Figure (3b-14)

AROMATIC DDE HYDRODECHLORINATION FAVORED AT LOWER HYDROGEN PRESSURES IN THE LIQUID PHASE

10% Pd on C 20-100°C



$$ka/ko = \frac{k_{65} + k_{62} + 2k_{61}}{2k_{63} + 2k_{62} + 2k_{61}}$$

These values also show that $k_{32} > k_{65}$. Since each term, as with the Aroclors, is a product of a surface reaction term and an adsorption equilibrium constant, either the aromatic reaction rate is increased with loss of olefinic chlorine or loss of olefinic chlorine allows for stronger adsorption of the aromatic ring by either steric or inductive factors.

In the Ni catalyzed experiments, the ratio of the aromatic to olefinic rate was sensitive to the reduction temperature of the catalyst. At a reduction temperature of 220°C and reaction pressure of 50 atm., the ratio of the total olefinic to aromatic rate constant varied between 7.5-4.8. Increasing the reduction temperature, at the otherwise identical conditions, reduced this ratio to 3.5 (aromatic rate increased).

As with the Pd catalyzed experiments, selectivities were insensitive to reaction temperature in the range of 20-100°C. In general Ni is more selective towards aromatic hydrodechlorination of DDE than Pd.

3. Simple power law kinetics do not describe the reaction of DDE with time during the Pd catalyzed batch experiments. Therefore, the effects of process variables such as catalyst loading, stirrer speed, hydrogen pressure, and reaction temperature were correlated based on initial DDE raction rate, $\Delta C/\Delta t = R^{o}$ as tabulated on the following page.

Run No.	T°C	P_{H_2} (atm)	R^o DDE (moles/liter min)
DDE 2	100	50	1.55×10^{-3}
DDE 3	100	50	1.21×10^{-4}
DDE 4	100	50	6.85×10^{-4}
DDE 5	60	50	5.35×10^{-4}
DDE 5R	60	50	6.55×10^{-4}
DDE 5R△1	50		
DDE 6	24	50	6.06×10^{-6}
DDE 7	22	5	1.18×10^{-4}
DDE 8	100	7	3.92×10^{-4}
DDE 9	24	20	3.08×10^{-5}
DDE 10	98	20	7.85×10^{-4}
DDE 11	80	50	2.47×10^{-4}
DDE 11R	81	50	6.33×10^{-4}

Three experiments, DDE 2,3,4 were made to determine the effect of Pd on C catalyst loading on the observed rate. All three experiments were conducted at 50 atm H_2 pressure, 100°C and initial DDE concentration of 2.53×10^{-2} moles/liter. Figure (3b-15) is a plot of initial DDE reaction rate vs. catalyst loading. Initial DDE reaction rate is not proportional to catalyst loading at low catalyst levels. Satterfield (1) has explained that this type of behavior is due to poisoning of some of the catalyst by impurities in the system. In this study the first .1 gm / liter appears to be deactivated in this way which places a lower limit on catalyst concentration. All subsequent Pd and Ni catalyzed experiments were conducted at catalyst loadings of 0.242 and 0.403 gm / liter respectively.

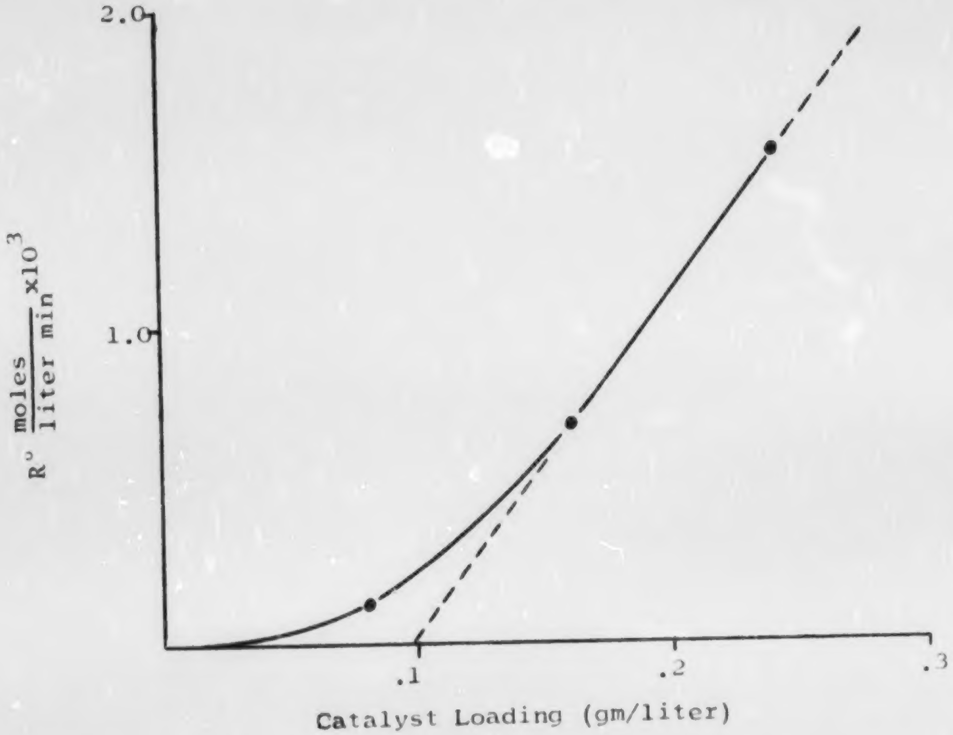
FIGURE (3b-15)

INITIAL DDE REACTION RATE AS A FUNCTION OF 10% Pd ON C CATALYST LOADING

50 Atm. H_2 Pressure

100°C

$C°_{DDE} = 2.53 \times 10^{-2}$ moles/liter



In experiments DDE 5R, 5RΔ1 stirrer speed was varied from 1500 to 900 RPM. No significant differences in initial rates or intermediate selectivities were observed indicating the absence of bulk mass transfer limitations over the range of speeds studied.

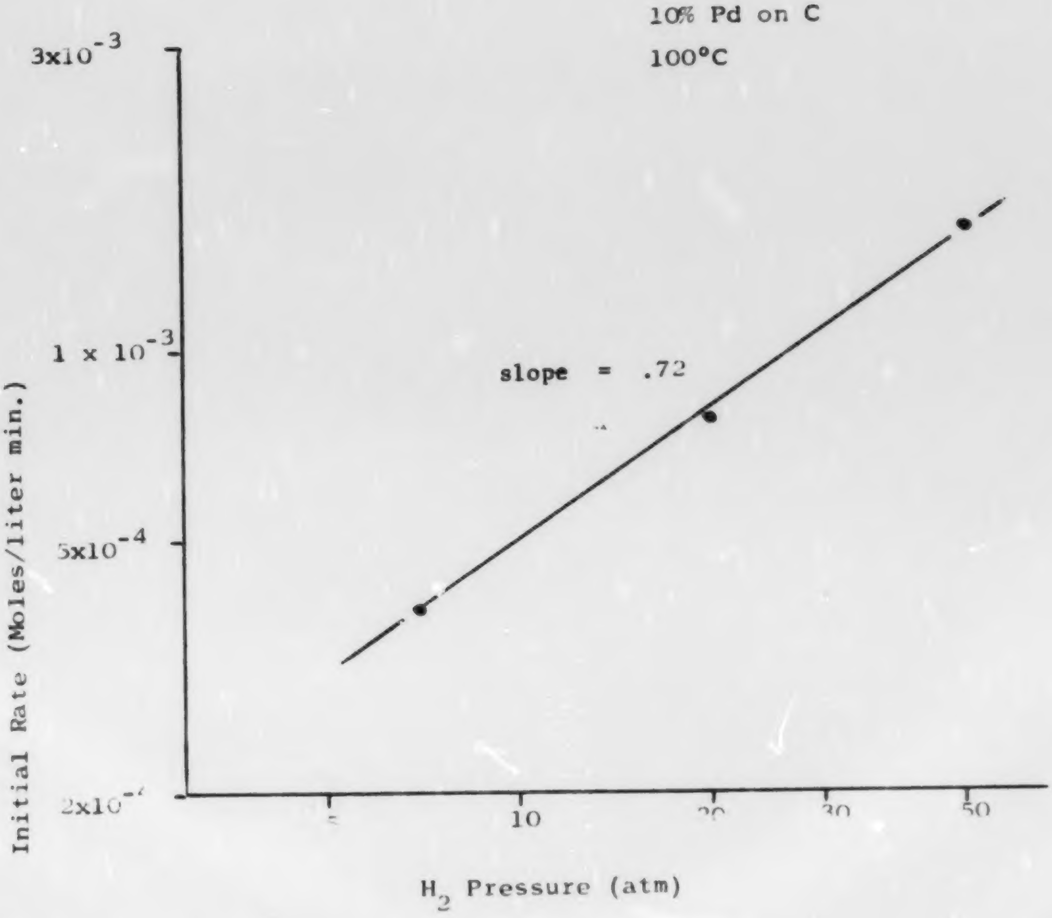
4. As stated previously, DDE reaction rates in both the Pd and Ni catalyzed experiments could not be described by simple power law kinetics.

In the Pd catalyzed experiments, attempts to fit DDE reaction behavior to a power law model gave the following results. As DDE conversion increased, apparent order in DDE increased from 1 to 2. Deviation from first order behavior at higher conversion is due either to product inhibition or catalyst deactivation. In these experiments, the catalyst was in contact with the reactant solution under a nitrogen atmosphere while the reactor was brought up to temperature. Therefore, deactivation due to the presence of the reactant itself should have occurred prior to the start of the experiment when the reactor was pressurized with hydrogen. The fact that the length of this prereaction period was a variable may account for the non-reproducible nature of the initial rates at identical conditions, e.g., DDE 5 vs. DDE 5R and DDE 11 vs. DDE 11R.

Experiments DDE 2, 10 and 8 were conducted at 50, 20 and 7 atm H_2 respectively, 100°C, and Pd catalyst concentration of 0.242 gm/liter to determine the effect of H_2 pressure on initial reaction rate. Figure (3b-16) is a log-log plot of initial rate vs. H_2 pressure which gave a +0.72 order H_2 dependence. The initial rates of experiments DDE 2, 5, 5R, 5RΔ1, 6, 7, 8, 9, 10, 11 and 11R were

FIGURE (3b-16)

DEPENDENCE OF INITIAL DDE REACTION RATE ON H_2 PRESSURE



divided by $P_{H_2}^{0.72}$ to determine the apparent activation energy for DDE reaction. Order of magnitude variance in the initial rates obtained at room temperature were observed but cannot be explained. Figure (3b-17) is an activation energy plot for these experiments which gave a value of E = 9.5 Kcal/mole.

The kinetic behavior of Ni catalyzed DDE hydrodechlorination is quite different from that observed in the Pd catalyzed experiments. DDE concentration vs. time curves are characterized by three regimes.

1. an induction period
2. zero order behavior at intermediate conversions
3. a shift to higher order functionality at high conversions

The G-49-A 61% Ni on Kieselguhr catalyst is prereduced and stabilized by the manufacturer. However, Ni on SiO_2 catalysts are notoriously difficult to reduce (2). In these experiments two reduction temperatures, 220°C and 370°C, were utilized. Figures (3b-18 , 19) are relative DDE concentration vs. time plots for experiments conducted at 50 atm. H_2 and temperatures from 40 to 100°C. Reduction temperatures are respectively 220°C and 370°C. In botn sets of experiments the length of the induction period decreases as reaction temperature increases.

	Induction Period (min.)	
Reaction Temp. (°C)	220°C Reduction	370°C Reduction
40	225	60
60	75	--
80	75	35
100	6	< 5

Figure (3b-17)

ACTIVATION ENERGY FOR Pd CATALYZED DDE HYDRODECHLORINATION

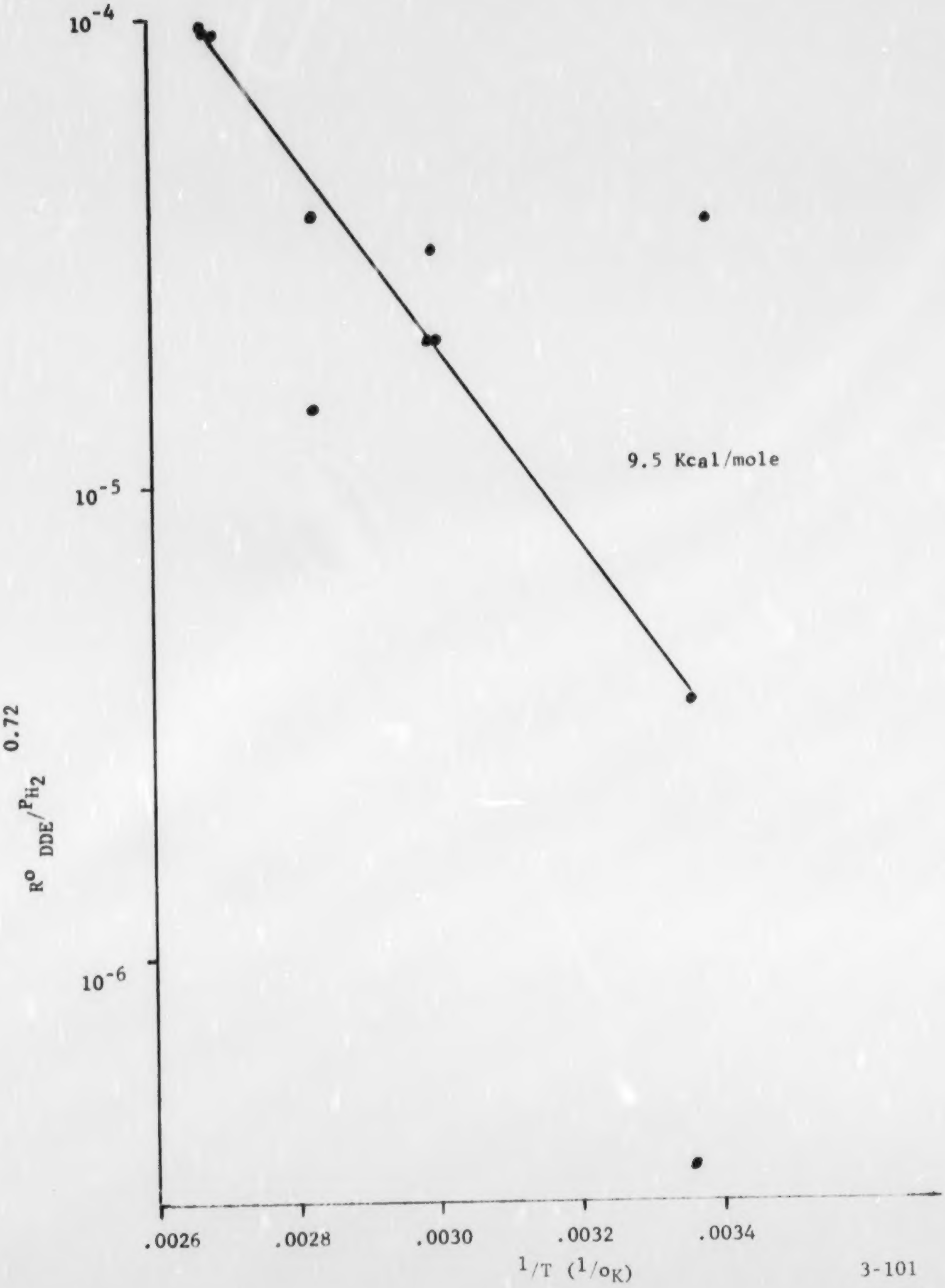


Figure (3b-18)

NI CATALYZED DDE KINETICS 220°C REDUCTION TEMPERATURE P_{H_2} = 50 ATM

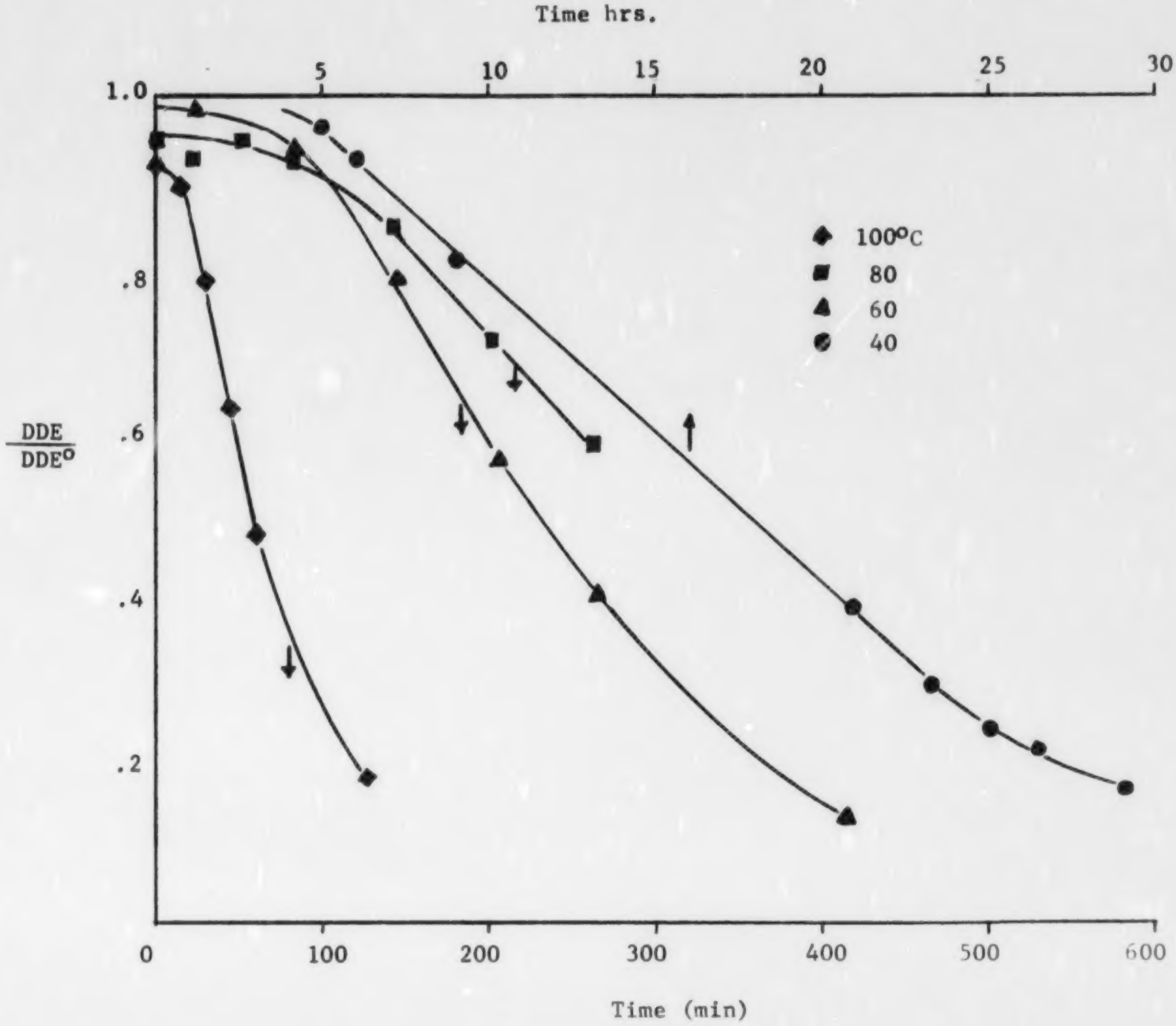
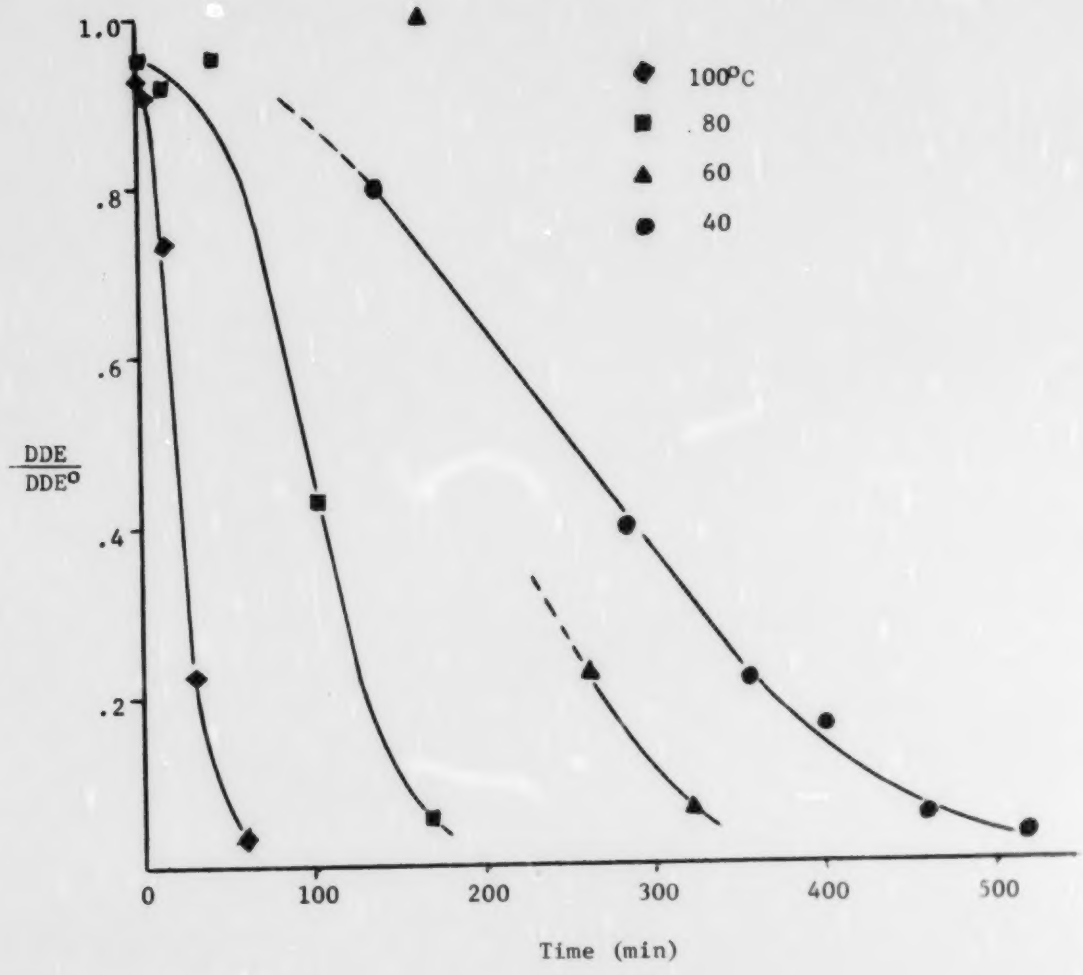


Figure (3b-19)

NI CATALYZED DDE KINETICS 370°C REDUCTION TEMPERATURE P_{H_2} = 50 ATM



Increasing the reduction temperature also decreases the length of the induction period. We believe this induction period is due either to continuing in-situ reduction of the catalyst as reaction proceeds, or is an indication of product desorption rate limitations as observed by Weiss et al. (3) in a homogeneously catalyzed system. Lack of this induction period in the Pd catalyzed experiments rules out the possibility of this effect being due to slow saturation of the liquid phase with hydrogen after the reactor was pressurized.

Zero order behavior at intermediate conversions is probably an indication that DDE is more strongly adsorbed on Ni than on Pd. The higher degree of concerted behavior at similar conditions is consistent with this observation as the possibility of multiple reaction steps occurring with a more strongly adsorbed substrate is favored.

At higher conversions a shift to higher order kinetics is expected as the surface concentration of strongly adsorbed reactants approaches zero. The apparent activation energy for the Ni catalyzed experiments where the catalyst was reduced at 370°C was determined from the zero order portion of the concentration vs. time curves.

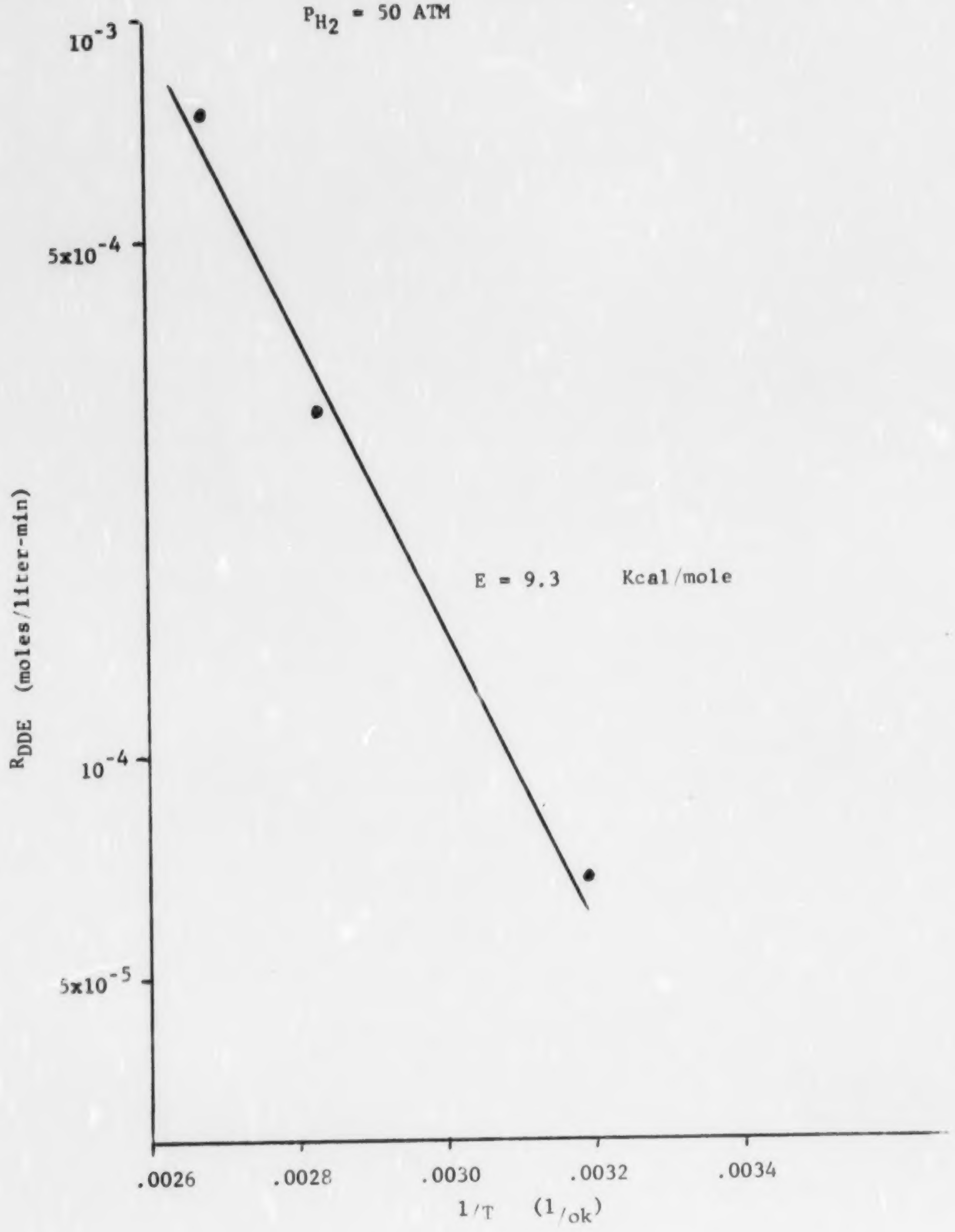
Run No.	T (°C)	P_{H_2} (atm)	Zero Order DDE Rate (moles/liter min)
	100	50	7.44×10^{-4}
	80	↓	2.94×10^{-4}
	40	↓	6.84×10^{-5}

These values yielded an apparent activation energy of E = 9.3 Kcal/mole, Figure (3b-20), as compared with 9.5 Kcal/mole for the Pd catalyzed experiments.

Figure (3b-20)

ACTIVATION ENERGY FOR Ni CATALYZED DDE HYDRODECHLORINATION

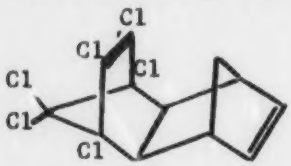
P_{H_2} = 50 ATM



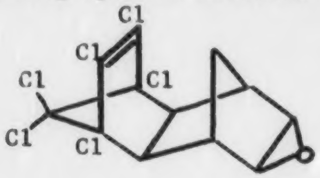
C. Aldrin, Dieldrin

Pulse microreactor and high pressure liquid phase reactions were carried out to determine the hydrodechlorination reactivity of Aldrin and Dieldrin which contain aliphatic and olefinic chlorine.

The structure of Aldrin and its corresponding epoxide Dieldrin are as follows:



ALDRIN



DIELDRIN

Technical grade samples of these insecticides obtained from The Shell Development Company's Biological Science Research Center, Modesto, Calif. are

Aldrin	Batch # 3-OCA-101
Dieldrin	Batch # 12-PCD-38

These were used in the liquid phase experiments while analytical grade chemicals obtained from Chem Service of West Chester, Pa. were used in the pulse microreactor screening.

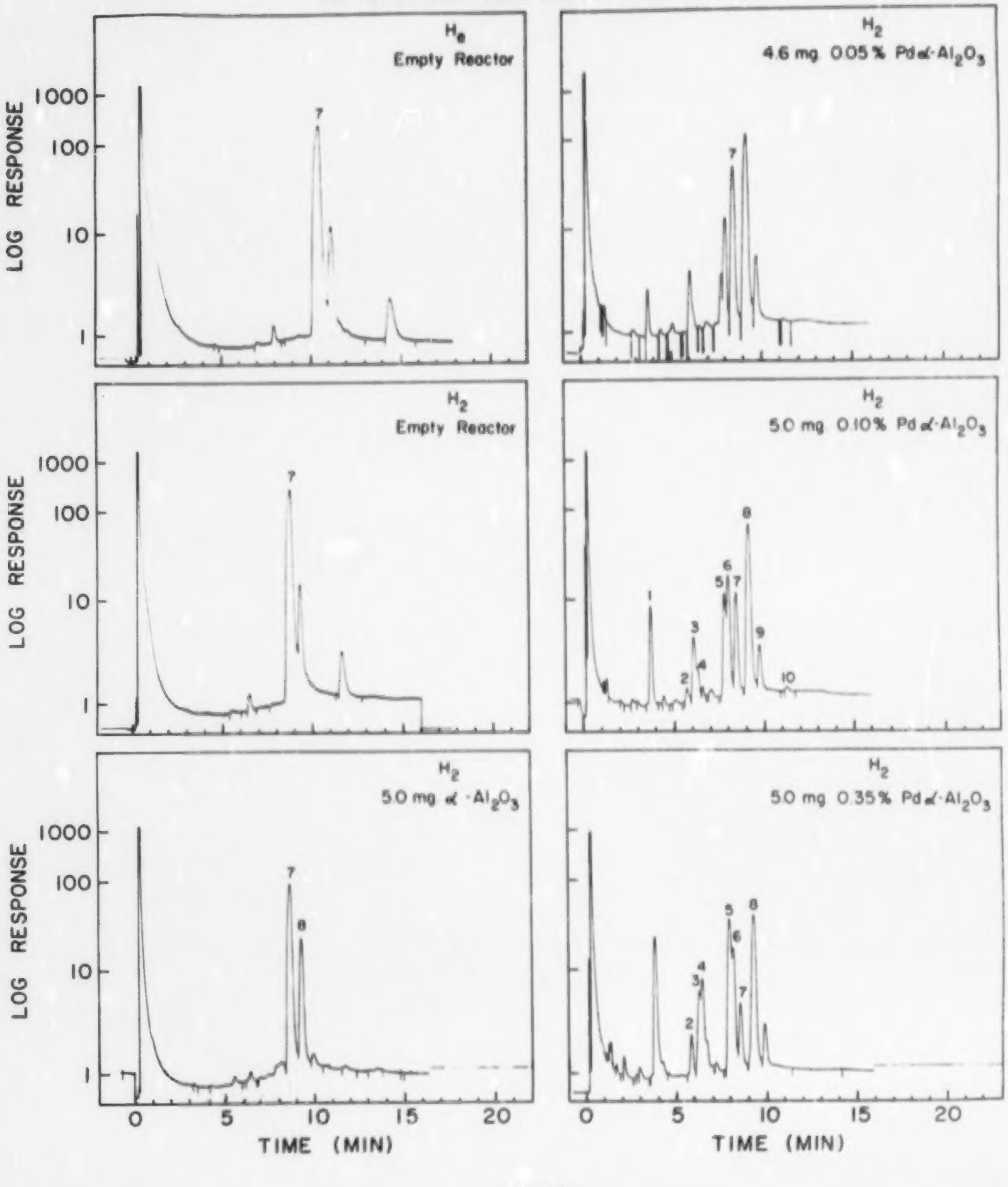
Gas Phase Pulse Microreactor Screening

A series of Aldrin hydrodechlorination experiments was carried out in the pulse microreactor at 220 ± 8°C and 2.3 atm absolute pressure using the same series of 0.00, 0.05, 0.10 and 0.35 wt% Pd on α - AL_2O_3 catalysts used in the Aroclor and DDT, DDD screening experiments. Figure (3C-1) is a set of log response chromatograms obtained in these experiments. This figure shows that no thermal hydrogenation / hydrodechlorination occured but that α - AL_2O_3 alone converted 11% of the Aldrin to a less volatile compound (later G.C./MS studies on liquid phase products showed this species to be Aldrin with one olefin hydrogenated). As Pd metal loading increased the extent of hydrogenation was

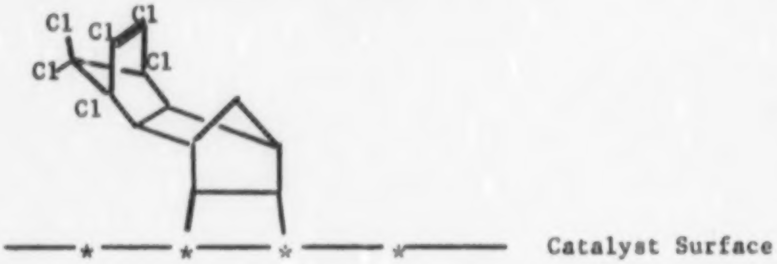
Figure (3C-1)

ALDRIN HYDRODECHLORINATION

30 SCC/Min. Gas, 220 ± 8°C, 19 PSIG



virtually quantitative while hydrodechlorination reactions proceeded in parallel. Table (3C-1) lists the analytical data for these experiments and is numerically cross referenced to Figure (3C-1). Figure (3C-2) is a reaction path which shows the extent of hydrogenation vs hydrodechlorination for these experiments. These data also indicate that Aldrin was the least reactive of all compounds studied in the pulse microreactor experiments. One pulse microreactor experiment was conducted to determine if this non reactivity was due to steric effects. Aldrin is a highly non planar molecule which may be adsorbed in such a configuration that hydrodechlorination reactions are not favored. Initial hydrogenation of an olefin may indicate that adsorption in the following configuration is favored.



However preliminary analysis of hexachlorocyclopentadiene hydrodechlorination which has a similar mix of aliphatic and olefinic chlorine indicate that this compound is much more reactive than Aldrin with concerted removal of all chlorine to a hydrocarbon species. This behavior may be due to the fact that this molecule can be adsorbed in a planar configuration so that hydrodechlorination reactions are favored.

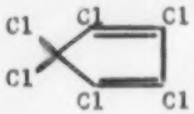


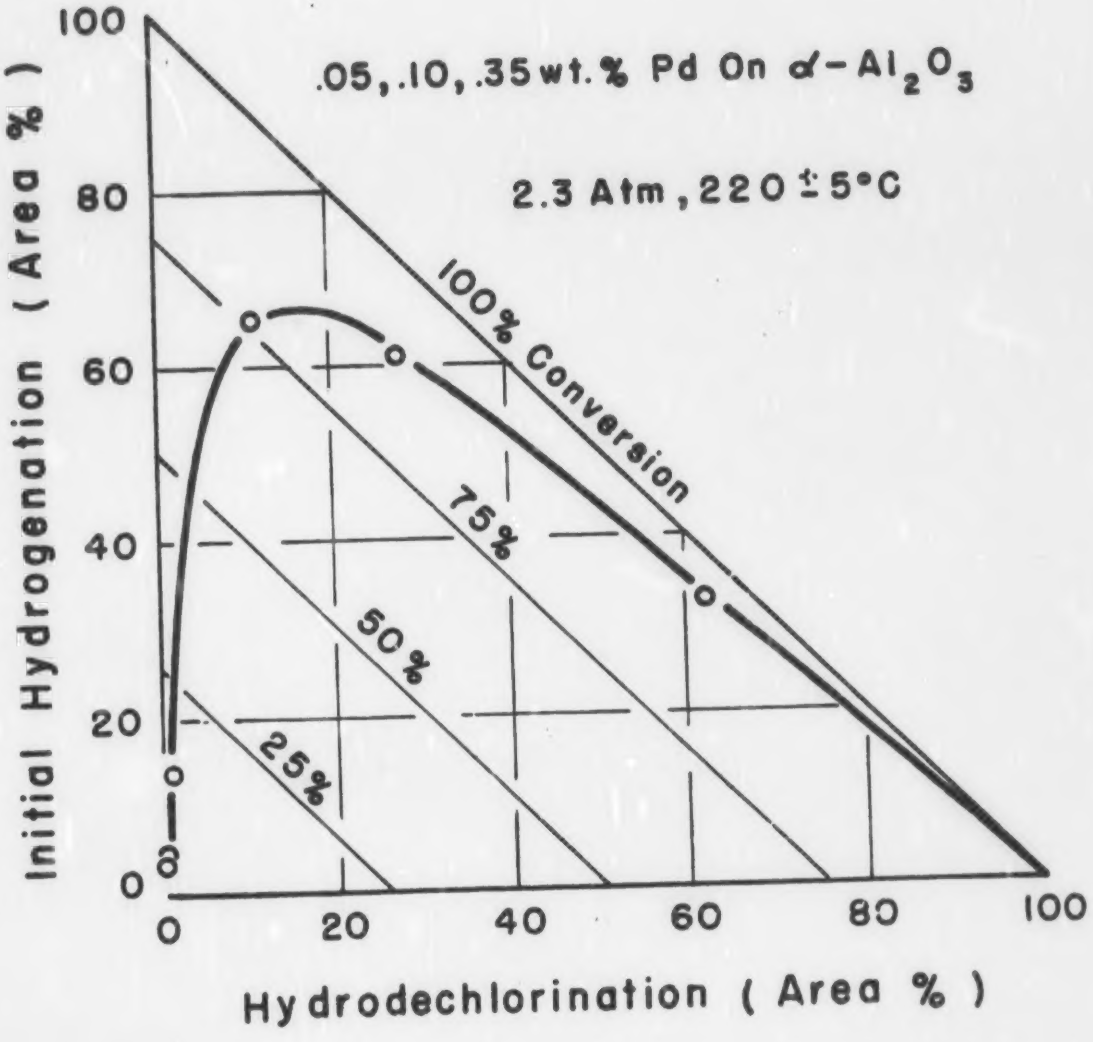
Table (3C-1)

ALDRIN HYDRODECHLORINATION

	Carrier Gas	He	H_2 →			
	Wt. of Catalyst	0	0	5.0mg	4.6mg	5.0mg	5.0mg
	Wt. % Pd			0.00	0.05	0.10	0.35
Identification	Compound No.			Area % Data			
↑	1				0.8	4.4	13.8
	2				0.1	0.4	1.1
Hydrodechlorination Products	3				1.8	3.7	3.5
	4				0.1	0.4	6.1
↓	5				1.3	6.7	27.7
	6			1.3	5.0	11.5	9.0
Aldrin	7	95.6	94.4	83.0	20.3	7.8	2.9
Aldrin + H_2	8	3.3	4.7	13.7	65.9	61.3	32.8
	9			1.2	3.7	2.8	1.9
	10	0.8	0.8	0.1	0.4	0.2	

Figure (3C-2)

ALDRIN REACTION PATH IN H_2



LIQUID PHASE EXPERIMENTS

An extensive set of preliminary liquid phase Dieldrin hydrodechlorination experiments was carried out in the rocking autoclave (see section II). All studies employed the N_i on Kieselguhr catalyst while pressure, temperature, time, and catalyst concentration were the major variables. Tables (3C-2,3) list the experimental conditions and condensed analytical results for these experiments. The major conclusion to be drawn from these experiments is that (1) only at very high catalyst loadings, reaction temperature, and hydrogen pressure were significant amounts of completely hydrodechlorinated product formed. i.e. 50 wt% catalyst, 175°C, and 750-1150 p.s.i. H_2 (2) Initial hydrogenation of the olefin was not observed which is consistent with the results obtained with DDE where hydrodechlorination is a precursor to hydrogenation.

Two additional experiments were carried out in the teflon autoclave under identical conditions to compare the reactivity of Aldrin and Dieldrin. Experimental conditions are listed below:

	EPA 4	EPA 5
Reactant	Aldrin	Dieldrin
Wt Reactant (GM)	2.0	2.0
Reaction Temp (°C)	130	130
H_2 Pressure (ATM)	50	50
Ethanol (GM)	98	98
Na(OH) (GM)	1.446	1.3853

Analytical data plus partial identification of major species are presented in tables (3C-4,5). Detailed kinetic analysis of these results has not been accomplished to date, however the following results are apparent.

Aldrin ($C_{12}H_8Cl_6$) initially reacts to produce a ($C_{12}H_{11}Cl_5$) species where one olefin has been saturated and one chlorine removed with high selectivity, i.e. 67 area % at 30 minutes reaction time, along with a broad spectrum of more highly dechlorinated products. Further reaction is characterized by the slow reaction of the $C_{12}H_{11}Cl_5$ species to produce $C_{12}H_{12}Cl_4$.

Table (3C-2)

LIQUID PHASE DIELDRIN EXPERIMENTAL CONDITIONS

Run #	4	10	7	11	13	14	3
Dieldrin (gm)	1.41	1.42	1.41	1.41	1.43	1.40	1.41
Dieldrin (moles)	.0037	.0037	.0037	.0037	.0038	.0037	.0037
Ethanol (g)	78.9	78.9	78.9	78.9	78.9	78.9	78.9
Wt. % Dieldrin	1.79	1.80	1.78	1.79	1.81	1.79	1.79
NaOH (gm)	1.041	1.417	1.391	1.419	1.410	1.393	1.046
NaOH (moles)	0.026	0.035	0.034	0.035	0.035	0.035	0.026
NaOH:Dieldrin	7.02	9.50	9.19	1.46	1.21	1.46	7.03
Wt. Nickel on Kiesulghr	0.142	0.144	0.149	0.143	0.140	0.140	0.699
Wt. Dieldrin / Wt. Catalyst	9.93	9.86	9.80	9.86	10.21	10.00	2.02
Reaction time (hrs)	1.5	3.0	4.5	1.5	1.5	1.5	1.5
Pressure (psi)	750-1150	750-950	750-1250	750-1975	360-700	155-350	750-1150
Temperature °C	25-180	24-181	25-181	25-300	25-183	25-180	25-175

Table (3C-3)

DIELDRIN PRODUCTS

Run#	Feed	4	10	7	11	13	14	3
0 Cl	0.00	1.80	9.45	12.44	11.37	0.00	0.33	49.37
1 Cl	0.00	7.96	28.09	21.98	8.05	3.77	5.76	34.20
2 Cl	0.26	3.73	5.43	6.92	0.00	0.00	0.36	0.00
3 Cl	0.15	16.17	8.62	32.12	34.05	10.70	2.46	1.17
4 Cl	0.00	36.33	21.28	21.41	33.68	1.12	1.29	6.84
5 Cl	0.00	33.73	27.12	0.00	9.11	84.24	89.18	9.23
6 Cl	96.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Average Cl Content	6.00	3.78	2.86	2.18	2.90	4.62	4.65	1.11
Cl conversion %		37.0	52.3	63.7	51.7	23.0	22.5	81.5

Table (3C-4)

EPA 4 ANALYTICAL RESULTS

ALDRIN HYDRODECHLORINATION

N_1 on K, 130°C, 50 ATM H_2

Reaction Time (min)	0	15	30	45	75	1035		
sample #	0	1	2	3	5	7		
R.T.(min)*								
4.4				.0016	.0018	.0020		
5.0			.0077		.0007	.0018		
8.8		.0016	.0122	.0137	.0149	.0275		
10.6		.0128	.0544	.0630	.0669	.0805	$C_{12}H_{16}Cl_2$	
12.6		.0069	.0114	.0134	.0141	.0369		
13.3	.004	.0167	.0127	.0073	.0048	.0129		
13.8			.0019	.0027	.0018	.0006		
14.1		.0227	.1279	.1453	.1480	.1553	$C_{12}H_{15}Cl_3$	
14.6				.0013	.0016	.0035		
15.0		.0822	.0737					
15.1				.0840	.1138	.3925	$C_{12}H_{12}Cl_4$	
15.3								
15.6	.953	.4417	.0025				$C_{12}H_8Cl_6$	ALDRIN
15.9		.0066	.0095	.0104	.0113	.0186		
16.2		.3637	.6706	.5369	.6019	.2593	$C_{12}H_{11}Cl_5$	
16.4							$C_{12}H_{10}Cl_6$	
16.6	.040	.0239						
17.1		.0187	.0225	.0203	.0184	.0044		
17.2								

* 9' x 1/8 3% OV-17 on Chromosorb W-HP 30 cc/min He 102-250°C @ 8°C/min

Table (3C-5)

EPA 5 ANALYTICAL RESULTS

DIELDRIN HYDRODECHLORINATION

N_i on K, 130°C, 50 ATM H_2

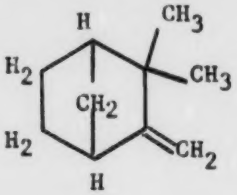
Reaction Time (min)	0	15	30	45	205	375	1380		
sample #	0	1	2	3	6	7	9		
R.T. (min)*									
12.3						.0147	SFS		
12.5					.0203	.0132	.0464		
13.8		.0284	.0596	.0758	.0818	.0879	.0975		
15.8	.0013	SFS	.0053	.0078	.0255	.0423	.0644		
15.9	.0107	.0328	.0222	.0124	SBS	SBS			
16.6				SFS	.0551	.0426	.1003		
16.7		.0292	.0698	.0819	.0739	.0722	.0569		
17.3	.0177	.0417	.0173	.0117					
17.5					.0073	.0151	.0139		
18.0		.0902	.3366	.4451	.6314	.6384	.5295	$C_{12}H_{10}Cl_4O$	
18.4	.9262							$C_{12}H_8Cl_6O$	Dieldrin
18.4		.7068	.4658	.3144	.0735	.0427	.0259	$C_{12}H_9Cl_5O$	
20.3	.0113	.0063	.0046	.0023					

* 9' x 1/8" 3% OV-17 on Chromosorb W-HP 30 cc/min He 102-250°C @ 8°C/min

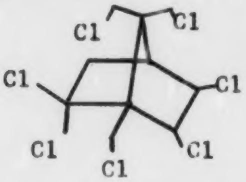
Dieldrin ($C_{12}H_8Cl_6O$) on the other hand is not hydrogenated initially but as with aldrin one chlorine is rapidly removed to give ($C_{12}H_9Cl_5O$) and a broad spectrum of more highly dechlorinated products. Further reaction is again characterized by a somewhat more rapid loss of an additional chlorine to give ($C_{12}H_{10}Cl_4O$) with high selectivity. Further reaction requires more severe conditions as mentioned earlier.

III-D Toxaphene (Polychlorinated Camphene)

Toxaphene is a mixture of polychlorinated camphene, containing typically 67-69% chlorine by weight, manufactured by Hercules Inc. (Wilmington, Del.). While the structure of camphene ($C_{10}H_{16}$) is:



Holmstead et al (4) have reported that over two thirds of the components of commercial toxaphene are $C_{10}H_{18}$-x Cl_x compounds where the olefin has been saturated during chlorination. A typical component which has been isolated from a representative toxaphene mixture (5) is a heptachlorobornane.



Therefore most of the chlorine in toxaphene is aliphatic in nature. Based on $C_{10}H_{18-x}Cl_x$, 68 wt % chlorine corresponds to $x=7.8$ chlorines/molecule. Smith (6) has calculated the number of possible toxaphene isomers assuming that the double bond could also be chlorinated. The following table presents Smith's calculation of the numer of chlorines containing n chlorines/molecule assuming no stereoisomers

n = number of chlorine	number of isomers
0	1
1	8
2	34
3	101
4	233
5	441
6	707
7	979
8	1185
9	1262
10	1185
11	979
12	707
13	441
14	233
15	101
16	34
17	8
18	1

As a result of this complexity quantitative analyses based on number of chlorines/molecule could not be obtained in all cases.

LIQUID PHASE EXPERIMENTS

A series of four experiments was conducted to determine the overall reactivity of toxaphene to catalytic hydrodechlorination. Tables (3D-1,2) respectively list the experimental conditions and our best estimate of product distribution data. At these conditions most of the chlorine was removed during the first two hours of reaction. Intermediates containing 1 and 2 chlorines per molecule appear to be resistant to further hydrodechlorination reactions. The major terminal product was identified as a $C_{10}H_{18}$ hydrocarbon. Of interest is the fact that toxaphene is more easily hydrodechlorinated than Aldrin or Dieldrin even though most of the chlorine is aliphatic in nature. This behavior further substantiates our belief that steric factors account for the non reactivity of Aldrin and Dieldrin. These same factors may account for the difficulty encountered in removing the last two chlorines from Toxaphene.

Table (3D-1)

LIQUID PHASE TOXAPHENE EXPERIMENTAL CONDITIONS

Run #	1	2	3	DR23
Wt. Toxaphene (gms)	2.0037	1.9861	2.0013	10.0
Ethanol (gms)	45.85	45.81	45.80	157.8
Wt. % Toxaphene	4.19	4.16	4.18	5.96
NaOH (gms)	1.5201	1.5251	1.5284	10% EXCESS
Wt. Catalyst (gms) Ni on Kieselguhr	.1976	.2013	.1989	1.000
$\frac{\text{wt. Toxaphene}}{\text{wt. catalyst}}$	10.14	9.87	10.06	10.0
Reaction time (hrs)	2 hrs	4 hrs	6 hrs	19 hrs
Pressure (Bar)	50	50(-52)	50(55)	50
Temperature (^{o}C)	100	97	100	100

Table (3D-2)

TOXAPHENE PRODUCT ANALYSIS

Reaction time(hrs)	2	4	6	19
# Cl/molecule				
0	16.67	32.43	30.12	36.6
1	21.64	29.03	27.03	25.5
2	30.17	20.27	13.41	23.9
3	9.45	2.74	12.79	1.2
4	8.64	11.62	5.02	10.4
5	5.55	1.98	1.91	1.1
6	6.22	1.94	3.85	
7	1.55			
8	1.16			

REFERENCES

1) Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis" M.I.T. Press Copyright 1970

2) Anderson, J. R., "Structure of Metallic Catalysts" Academic Press London Copyright 1975

3) Weiss, A. H., LaPierre, R. B., and Shapira, J., J. Catal. 16, 332 (1970)

4) Holmstead, R. L., Khalifa, S., and Casida, J. E., J. Agr. Food Chem., Vol. 22, No. 6, 1974

5) Casida, J. E., Holmstead, R. L., Khalifa, S., Knox, J. R., Ohsawa, T., Palmer, K. J., Wong, R. Y., Science 183, 520 (1974)

6) Smith, D. H., Anal. Chem., Vol. 47, No. 7, June 1975

IV PROCESS DESIGN

Although the final design of a hydrodechlorination process is beyond the scope of this project, many of the problems of such a design can be approached with the aid of the data obtained. The process design involves both qualitative aspects - choice of process step and equipment type - and quantitative aspects - size, temperature, pressure, time, etc.

BATCH OR CONTINUOUS PROCESS

Successful operation of continuous processes is best achieved when a steady flow of a feed of uniform composition is available. In the problem of pesticide disposal, the chemical is variable, perhaps even unknown. In addition the quantity is uncertain, solvents and extenders are variable and packaging is uncertain. In some cases the objective may even be to clean pesticide residues from cans or cartons before incineration or land fill dumping.

A batch process, at least in the initial stages of process development, is clearly indicated.

LIQUID OR GAS PHASE

Although we have been successful in the gas phase hydrodeclorination of some of our model compounds, we foresee problems because of varying volatility of feeds of different composition, the need for very high temperatures for vaporization of some of the compounds, and the accompanying thermal degradation of some of the reactants or products with formation of tar or coke on the catalyst.

Liquid phase reaction in solvent is recommended.

CHOICE OF SOLVENT

We have looked at non-polar solvents such as xylene and polar solvents such as ethanol. While xylene is an excellent solvent for the aromatic pesticides it is a relatively poor solvent for the acid acceptor, which is needed to reduce corrosion and produce a non-polluting effluent. Furthermore, it has some effect in lowering the rate of hydrodechlorination of aromatics since it behaves like a reaction product.

Hot ethanol is a reasonably good solvent for the chemicals being treated and for the products formed. Other alcohols and diols were also investigated. The higher alcohols have the advantage of lower vapor pressure (and therefore of contributing less to the total pressure which must be confined within the reactor.) On the other hand their separation and recovery by distillation is more difficult and they are in general more costly.

Ethyl alcohol is selected as solvent.

OPERATING TEMPERATURE

Operation at high temperature results in more rapid solution of the solid pesticides, greater solubility (with resulting reduction in size of equipment and amount of solvent) and more rapid reaction. On the other hand, obviously more heat is required and the total pressure needed for a particular hydrogen partial pressure is increased.

Initial extraction of the pesticides into ethanol solution is suggested at atmospheric pressure and close to the boiling point. Hydrodechlorination at about 100°C is recommended. Materials more resistant to hydrodechlorination, such as dieldrin and aldrin may require higher temperature.

OPERATING PRESSURE

The extraction (solution) step should be carried out at about atmospheric pressure to reduce the complications of equipment design and operation. The hydrodechlorination step requires elevated hydrogen pressure to attain reasonable reaction rates. A partial pressure of hydrogen of 20-50 atmospheres is recommended.

CATALYST

The Girdler G 49A nickel on kieselguhr catalyst used in these studies is satisfactory for both economic and activity reasons.

For plant operation particles as large as 1/16-1/8 inch in diameter, to allow for ready retention in the reactor by a stainless steel screen are indicated.

Catalyst life under service conditions has not been determined. It may be expected to vary considerably with the nature of the feed, impurities, and the severity of reaction conditions. Catalyst life and ease of regeneration will figure importantly in economic considerations.

ACID ACCEPTOR

Although it is possible to operate with HCl as a byproduct, this acid is highly corrosive and is unacceptable as a vented waste product.

In this study NaOH and $Ca(OH)_2$ were investigated as acid acceptors (neutralizers). Sodium hydroxide gave far superior results because of its solubility in ethanol, and is recommended.

The byproduct NaCl can be washed away from the product with water. Under most circumstances it can be sufficiently diluted for acceptable disposal.

PRODUCT RECOVERY

Details of product recovery depend on the nature of the feed and the severity of processing. In many cases the product will be a reasonably pure organic liquid suitable for refining and use as a raw material.

Where the product is a complex mixture of completely hydrodechlorinated hydrocarbons mixing with fuel oil and burning in a furnace may be indicated. Where chlorine residues are small but significant, burning in a municipal incinerator may be indicated.

In some cases the products may be solids acceptable for landfill dumping.

PROCESS DESCRIPTION

A conceptualized flow sheet for a suitable process is given in Figure (4,1).

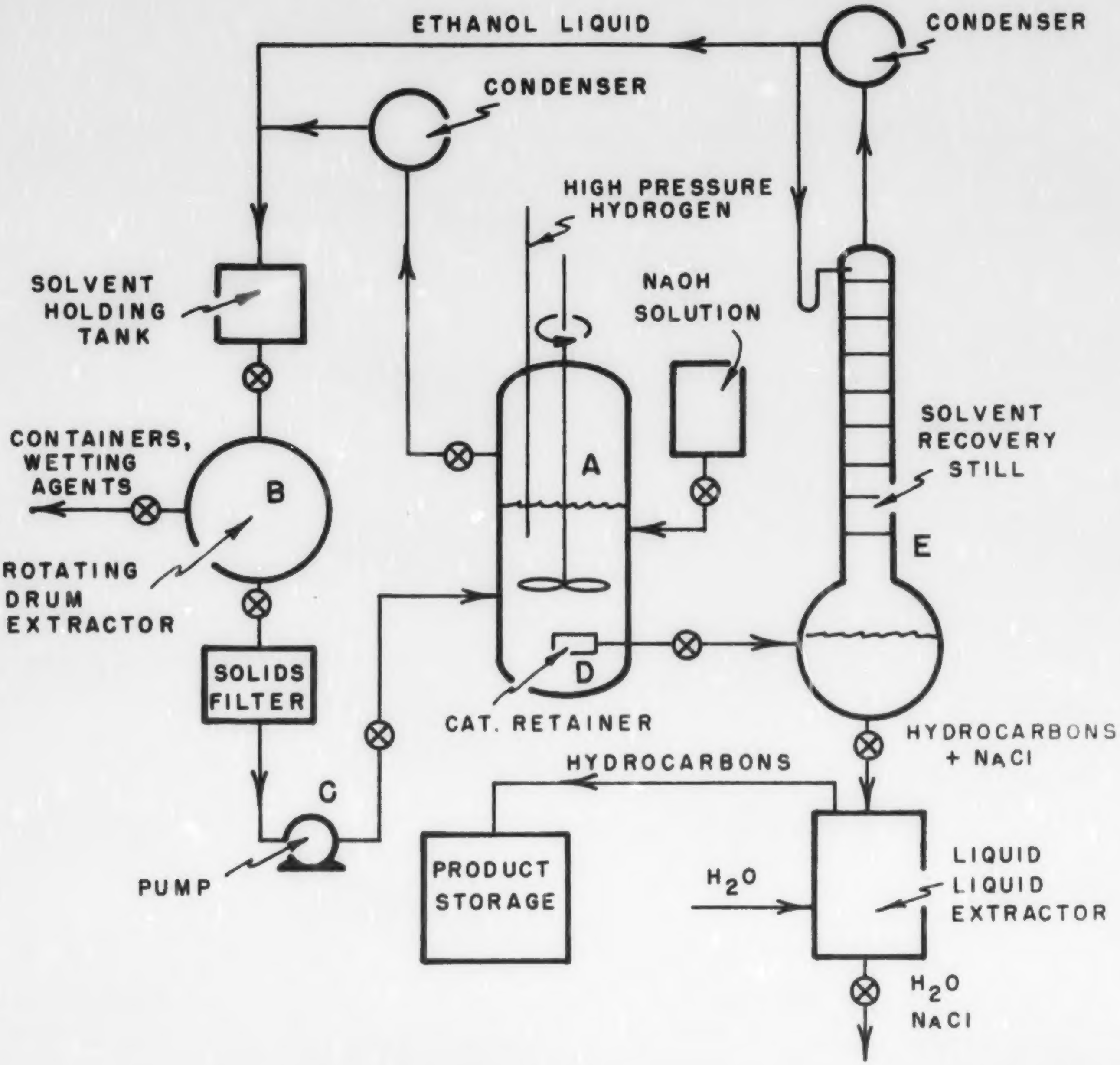
The materials to be treated are charged as a batch to a rotary (tumbling) extractor(B). The organic materials to be hydrodechlorinated are extracted with hot ethanol and pumped (C) to the main reactor(A). During the extraction phase the reactor contents are boiled at atmospheric pressure and the ethanol is evaporated, condensed and returned to the extractor until the containers and inert materials remaining in the extractor are free of pesticides. (The principle of operation is similar to that of the Soxhlet extractor in traditional organic chemistry laboratories)

Sodium hydroxide (dissolved in ethanol) is then added to Reactor A and the system is pressurized with hydrogen. Hydrodechlorination proceeds in the presence of the nickel catalyst retained in the reactor.

When the reaction is complete the liquid contents are strained through the catalyst retention screen to the solvent recovery Still E. Here some or all of the ethanol is boiled off, purified in a column and returned to the solvent holding tank. (In an alternative arrangement, most of the ethanol may be recovered by boiling from the reactor itself and Still E eliminated.) Such a simplified system would require careful study of solubilities, recoveries and expected compositions of feeds and products.

The products containing NaCl and excess NaOH are extracted with water to remove the soluble inorganics. Use or disposal of the organic products depends on the degree of dechlorination, complexity of the feed and product, and the usefulness of the product for other purposes.

Figure (4-1)



PESTICIDE DETOXIFICATION PROCESS FLOW SHEET

V ANALYTICAL TECHNIQUES

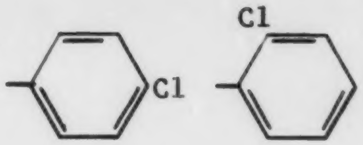
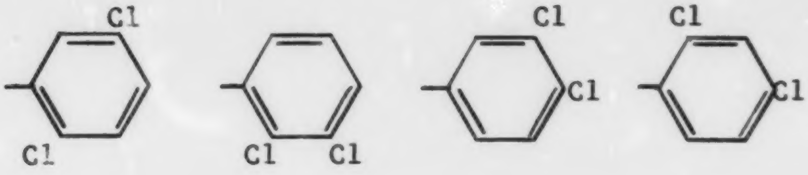
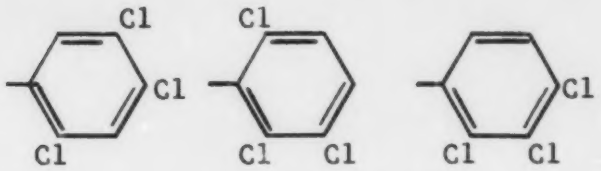
GC-MS techniques were used for identification and quantitative analysis of all reactants and products studied during the course of these investigations on the hydrodechlorination of pesticides and related substances. The equipment used were a Perkin-Elmer 900 dual flame ionization detector gas chromatograph interfaced with a DuPont 21-491 double focusing mass spectrometer; a CSI model 208 automatic digital integrator was used for quantitating FID output. Mass spectra were recorded using a CSI 5-124A recording oscillograph. Molecular weight determination and structural information obtained from the mass spectra of individual chromatographic peaks identified reaction intermediates in the complex systems studied. The carbon counting flame ionization detector gave quantitative conversion and rate data.

V-A AROCLOR ANALYSIS

Smith (1) has calculated the total number of polychlorinated biphenyl (PCB) isomers to be 210. The number of possible isomers containing n chlorine atoms per molecule is as follows:

n	No. of Isomers
0	1
1	3
2	12
3	24
4	42
5	46
6	42
7	24
8	12
9	3
10	1

Hutzinger, Safe & Zitko (2) report that the most common substitution pattern for PCB's are as follows:

# cl/ring	most common substitution pattern
1	
2	
3	

with rough equivalence of the number of chlorines on each ring, (e.g., very little trichlorobiphenyl with 3 chlorine atoms on one ring and none on the other is found). Even these simplifications, however, make PCB analysis difficult. The approach used in this work for characterizing Aroclor 1248 and its hydrodechlorination products is by number of chlorine atoms/molecule and total ortho vs. total meta + para substitution within each group containing the same number of chlorine atoms/molecule Details of the analyses follow:

Pulse microreactor and preliminary liquid phase reaction products were separated on a 5' x 1/8" 3% OV-1 on Chromosorb W HP column. Later samples were analyzed on a 9' x 1/8" 3%

OV-17 on Chromasorb W-HP column which gave better separation and could be operated up to 250°C without significant column bleed. A 6' x 1/8" 3% SE-30 on Chromosorb W HP column was used to reproduce the results of Webb et al, (3) on the identification of individual PCB isomers. Both OV-1 and SE-30 are methyl substituted silicone gums with similar characteristics while OV-17 is 50% phenyl and 50% methyl substituted silicone gum.

The mass spectra of a number of individual isomeric chlorobiphenyls (PCB's) have been reported (4,5) and summarized by Safe and Hutzinger (6). In general the E.I. mass spectra of PCB's are characterized by intense molecular ions and elimination of 2 chlorine atoms from biphenyl containing two or more chlorine atoms per molecule. The primary ion mass spectra of isomeric species are virtually identical except that highly ortho substituted PCB gives more intense M-70 fragments.

The Aroclor 1248 used in these studies, obtained from Monsanto, was a viscous clear liquid containing 48% chlorine by weight. By using the OV-17 column, GC-MS identifications of all but the most trace components were obtained. Figure (5a-1) is a chromatogram of the Aroclor 1248 with the number of chlorines per molecule as identified by the observed molecular ions. Based on these data, break points between groups of peaks containing the same number of chlorine atoms per molecule were chosen, although some overlap was observed. Table (5a-1) lists retention time, number of chlorine/molecule as identified by GC-MS, and area % of each peak in the Aroclor 1248. Since area % with FID is equal to mole % of biphenyl nuclei, this analysis

Figure (5A-1)

AROCLOR 1248 CHROMATOGRAM

9' x 1/8" 3% Ov-17 on Chromasorb W-HP

122-250°C @ 5°C/min He 30 cc/min

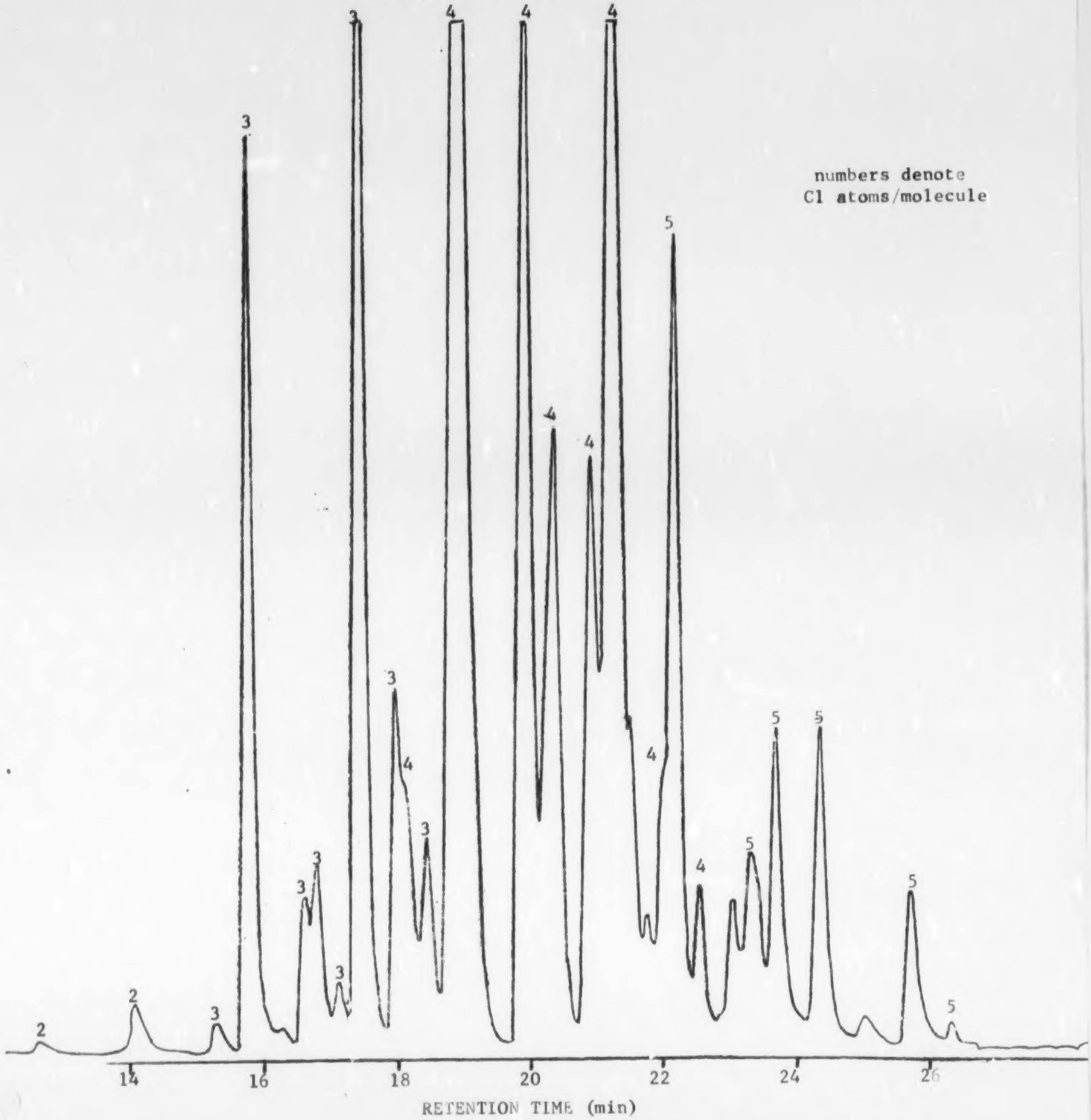


Table 5A-1

OV-17 AROCLOR 1248 ANALYSIS

OV-17* RT	No.Cl/Molecule by MS	Area %	Total Area % by No.CL/Molecule
5.0	0		
6.8	0		
9.8	1	.0009	.0009
11.2	1		
11.3	1		
12.4	2	.0015	.0067
13.0			
13.5	2	.0052	
13.8			
15.1	3	.0025	.2593
15.7	3	.0658	
16.2		.0021	
16.5	3	.0099	
16.7	3	.0144	
17.0	3	.0054	
17.4	3	.0993	
17.9	3	.0422	
SBS	4		
18.4	3	.0177	
18.8	4	.1768	.5321
19.1			
20.0	4	.0926	
20.4	4	.0625	
20.9	4	.0470	
21.3	4	.1446	
21.8		.0086	
SFS	4		
22.3	5	.0785	.2009
22.6	4	.0130	
23.1		.0131	
23.4	5	.0209	
23.7	5	.0283	
24.4	5	.0274	
25.0		.0035	
25.7	5	.0131	
26.1	5	.0031	
Total Area %		.9999	

* 9' x 1/8" 3% OV-17 on Chromosorb W HP, 30CC/min He, 122-250°C @ 5°C/min

corresponds to an average of 3.925 chlorine atoms/molecule or an average molecular weight of 289.2 ($C_{12}H_{6.075}Cl_{3.925}$) as compared to the 3.90 and 288 figures reported by Safe and Hutzinger (4). This good agreement illustrates how the F.I.D. behaves as a carbon counter and is insensitive to chlorine content.

As a further check on the observation, a mixture containing a molar ratio of Aroclor 1248 (MW 288) to biphenyl (MW 154) of 22.17 was analyzed. The observed chromotographic peak area ratio was 21.19, or a molar response ratio for biphenyl/aroclor 1248 of .956.

The linearity of the FID response was confirmed for both biphenyl and Aroclor 1248 up to .3 and .15μmole levels respectively, even though column overloading was observed at the largest sample sizes (Fig 5a-2). Analysis of Aroclor 1248 reaction products was carried out at the .076μmole level well within the linear range of the analysis.

Webb et al. (3) have identified the major components of Aroclor 1221 - 1254 using a 100' x .02" SE-30 SCOT column. A 6' x 1/8" 3% SE-30 on Chromosorb W HP column was constructed in the WPI laboratory and the analysis compared to that obtained by Webb. The packed column was not as efficient as the SCOT column. However, the corresponding peaks could be easily identified. Figure (5a-3) is a plot of the relative retention times obtained by Webb vs. WPI analysis.

Figure (5a-2)

LINEAR FID RESPONSE FOR AROCLOR 1248 AND BIPHENYL

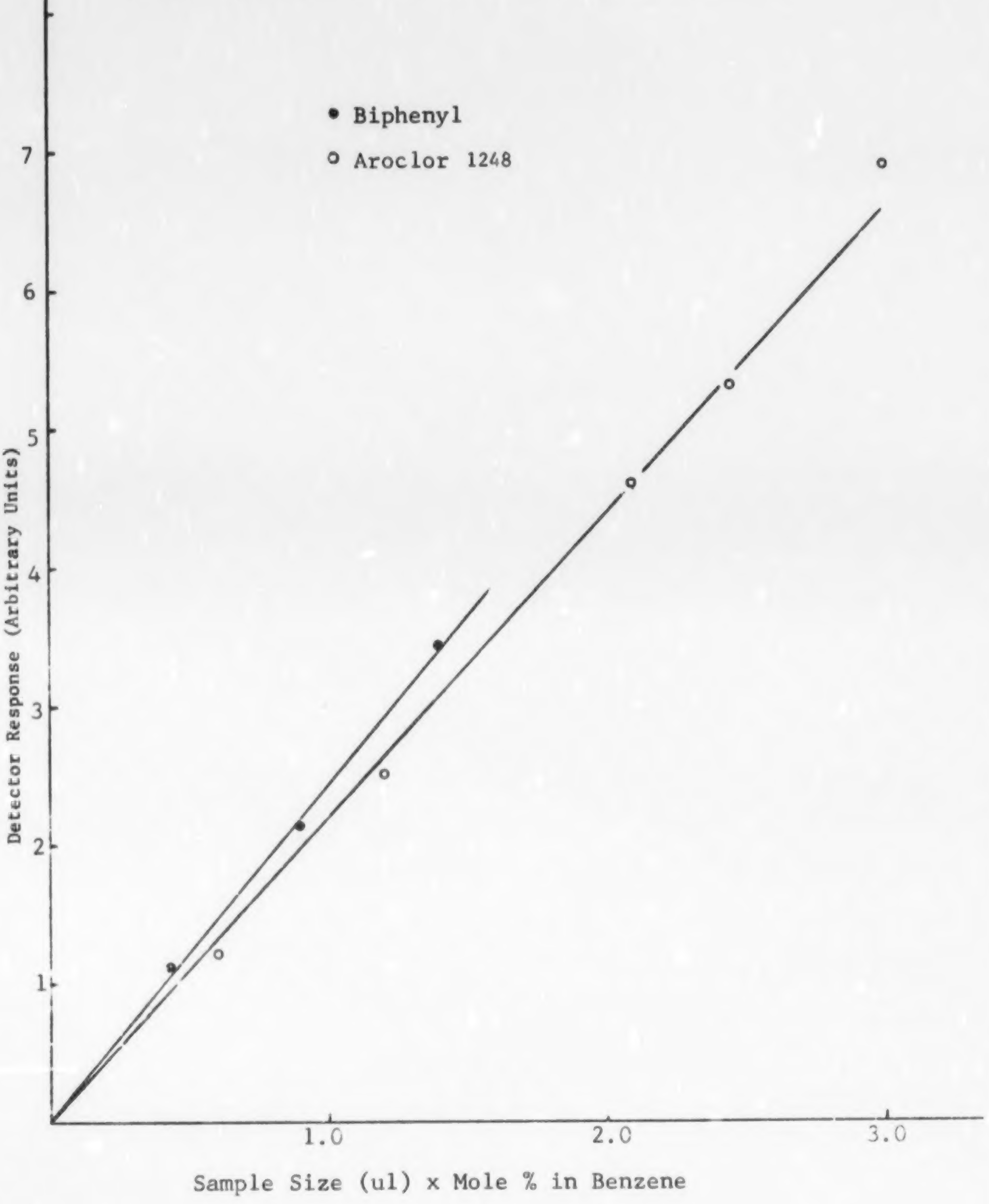


Figure (5A-3)

COMPARISON OF 100' x .02" SCOT vs 6' x 1/8" PACKED SE 30

AROCLOR RETENTION TIMES

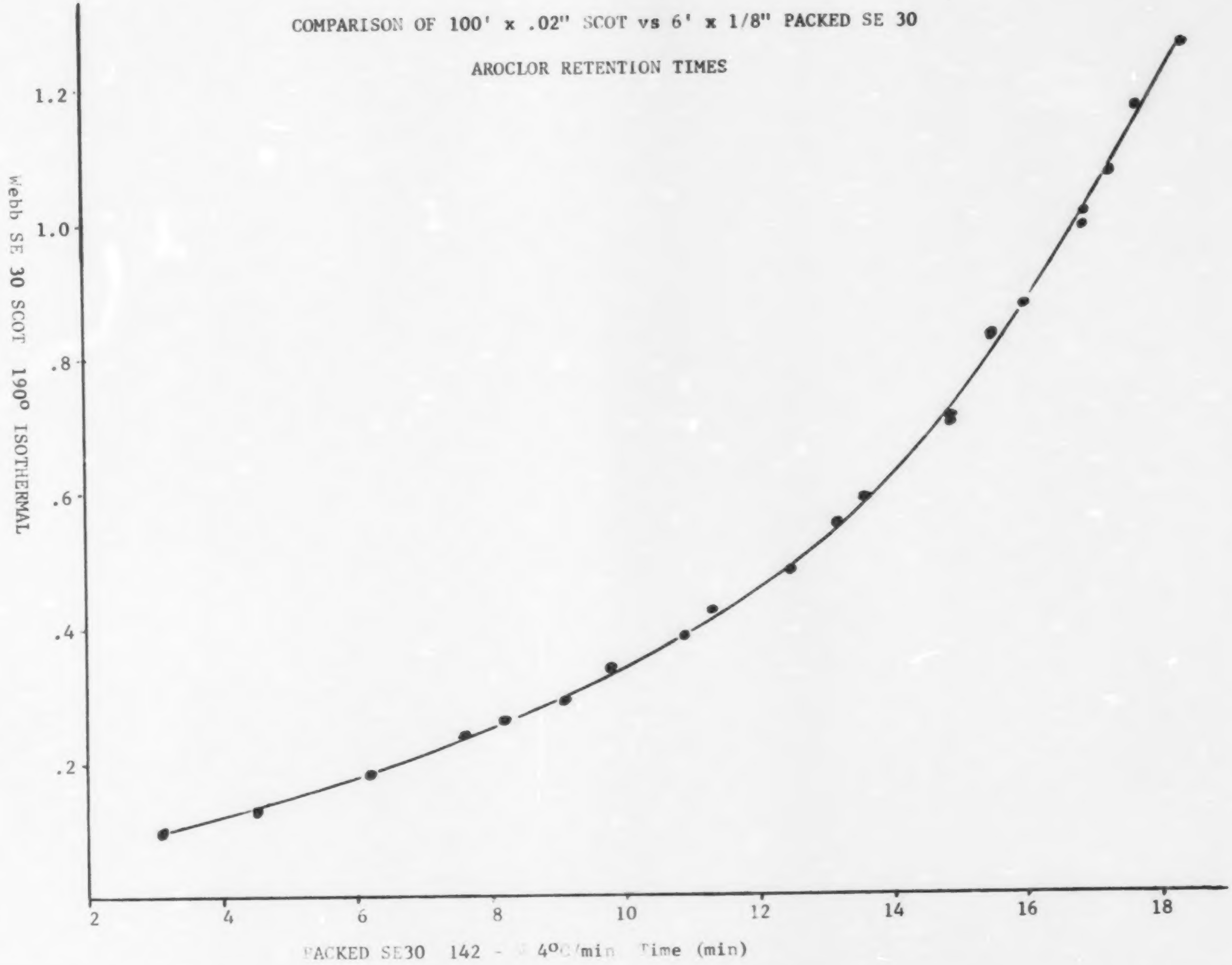


Table (5a-2) is a synthesis of the results obtained by Webb and this present work using the 6' x 1/8" SE 30 packed column. In this way one can characterize not only the average number of chlorines/molecule (3.91 by this analysis) but also the % ortho vs. total % meta + para isomers based on the major species identified by Webb. Table (5a-3) cross references, the SE 30 and OV-17 analyses. Overall agreement between the two analyses was obtained although minor differences were noted, especially in the 4 and 5 chloro isomers.

Table 5A-2

SE 30 AROCLOR 1248 ANALYSIS

Identification Webb et al	Retention Time (min) 6'x1/8" SE 30 142 → @ 4	No.O-Cl	No.M,P-Cl	n	Relative Area
Biphenyl	3.1	0	0		
2	4.5	1	0		.0009
3+4	5.7	0	1		.0002
2,2'	6.2	2	0		.0015
?	7.1	1	1 Est		.0002
2,3'+2,4'	7.6	1	1		.0047
2,2',6	8.2	3	0		.0024
2,2',5+2,2',4+4,4'	9.1	2	1		.0667
2,2',3	9.8	2	1		.0259
2,3'4+2,4,4'+2,4',5	10.9	1	2		.1053
2',3,4	11.3	1	2		.0737
2,2',5,5'+2,2',4,5'+2,2'4,4'	12.5	2	2		.1584
2,2',3,5'	13.2	2	2		.0947
2,2',3,6,6'	13.6	4	1 (2,2)*		.0741
2,3',4'5+2,3'4,4'	14.9	1	3		.1856
2,2',3,3',6	15.5	3	2		.0629
2,2',4',4,5	16.0	2	3		.0332
2,2',3',4,5	16.9	2	3		.0327
2,3,3',4',6	17.3	2	3		.0296
?	17.7	1	4 Est		.0056
2,3',4,4',5	18.4	1	4		.0239
?	19.4	1	4 Est		.0149
?	20.5	1	4 Est		.0022
?	21.5	1	4 Est		.0005
					.9998
	Total O	1.647			
	Total M,P		2.2676		
	Total Cl	3.9146			

* 4 Cl compound by GC, MS

Table 5A-3
COMPARISON OF OV 17 AND SE 30 AROCLOR 1248 ANALYSES

9'x1/8" OV 17 122-250 @ 5	Relative Area	6'x1/8" SE 30 142— @ 4	Relative Area	# O	# M,P	
6.8		3.1		0	0	
9.8	.0009	4.5	.0009	1	0	
11.2+11.3		5.7	.0002	0	1	
12.4	.0015	6.2	.0015	2	0	
13.0		7.1	.0002	1	1	Est
13.5+13.8	.0052	7.6	.0047	1	1	
15.1	.0025	8.2	.0024	3	0	
15.7+16.2	.0679	9.1	.0667	2	1	
16.5+16.7	.0243	9.8	.0259	2	1	
17.0+17.4	.1047	10.9	.1053	1	2	
17.9+18.4	.0599	11.3	.0737	1	2	
18.8+19.1	.1768	12.5	.1584	2	2	
20.0	.0926	13.2	.0947	2	2	
20.4	.0625	13.6	.0741	4	1	(2,2)
20.9+21.3	.1916	14.9	.1856	1	3	
21.8+22.3	.0871	15.5	.0629	3	2	
22.6+23.1	.0261	16.0	.0332	2	3	
23.4	.0209	16.9	.0327	2	3	
23.7	.0283	17.3	.0296	2	3	
		17.7	.0056	1	4	Est
24.4	.0274	18.4	.0239	1	4	
25.0+25.7	.0166	19.4	.0149	1	4	Est
		20.5	.0022	1	4	Est
		21.5	.0005	1	4	Est

OV 17	SE 30
Total O = 1.6769	Total O = 1.647
Total M,P = 2.2413	Total M,P = 2.2676
Total Cl = 3.9182	Total Cl - 3.9146

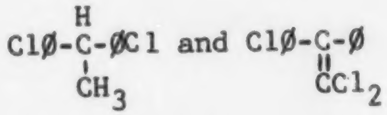
V-B 1,1 DIPHENYL ETHANES/ETHYLENES (DDT, DDE, DDD)

Two different chromotograph columns were used for analysis of chlorinated 1,1 diphenyl ethane/ethylene reactants and products. Pulse microreactor data and some preliminary liquid phase experiments used a 5' x 1/8" 3% OV-1 on Chromasorb W HP column. The bulk of the gas and liquid phase kinetic study reaction products were analyzed on a 9' x 1/8" 3% OV-17 on Chromasorb W HP column which was more appropriate for this analysis since this liquid phase is characterized by 50% phenyl substitution. The assumption that FID response was insensitive to chlorine content was checked by analyzing a mixture containing 3.14 mole % 1,1 diphenyl ethane and 3.88 mole % DDE in P-Xylene, or a molar ratio of DDE to 1,1 diphenyl ethane of 1.24. The observed corresponding area % ratio for several sample sizes was then determined.

Sample Size 1	Area % DDE / Area % 1,1 Diphenyl Ethane
0.10	1.16
0.20	1.17
0.25	1.18
0.40	1.08
0.60	1.20
0.80	1 18

In this way an average relative response factor for DDE relative to 11 diphenyl ethane of 0.95 was determined which agrees well with the 0.956 value determined for Aroclor 1248 containing an average of 3.92 chlorine atoms/molecule vs. biphenyl. Thus the attenuation per chlorine molecule is 1.25% which does not introduce serious error into the area % assumption.

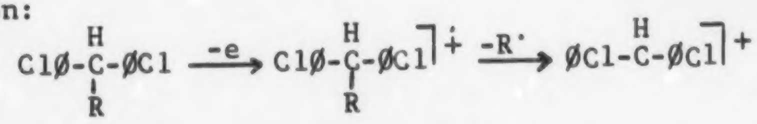
The mass spectra of a number of 2-chloro substituted 1,1 - bis - (p-chlorophenyl) ethanes and ethylenes have been reported (6,7) and the spectra of the corresponding hydrocarbons are available (8). However, neither authentic samples nor mass spectra of reaction intermediates produced in this study, such as



$$\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}\emptyset Cl} \quad \text{and} \quad \mathrm{Cl\emptyset\text{-}\underset{\overset{\|}{CCl_2}}{C}\text{-}\emptyset}$$

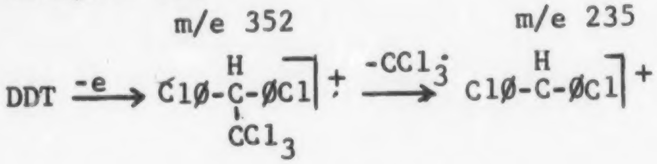
for example, were available.

The procedures used in identifying these compounds is as follows: The initial fragmentation of every reported 1,1 - bis - (p-chlorophenyl) ethane is characterized by the following reaction:

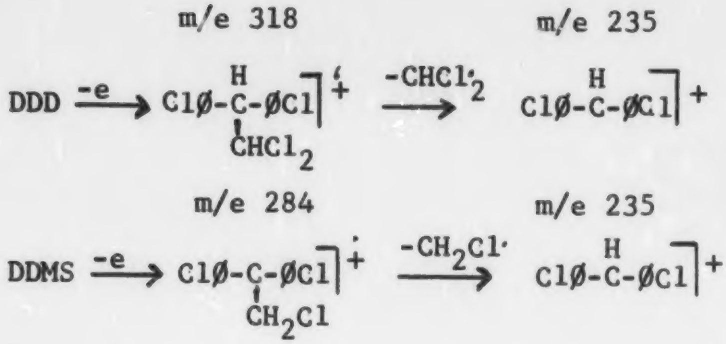


$$\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{R}{C}}\text{-}\emptyset Cl} \xrightarrow{-e} \left.\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{R}{C}}\text{-}\emptyset Cl}\right]^{\dot{+}} \xrightarrow{-R\cdot} \left.\mathrm{\emptyset Cl\text{-}\overset{H}{C}\text{-}\emptyset Cl}\right]^{+}$$

which yield the major fragment in the mass spectra and is followed by subsequent concerted removal of aromatic chlorine. Several examples are



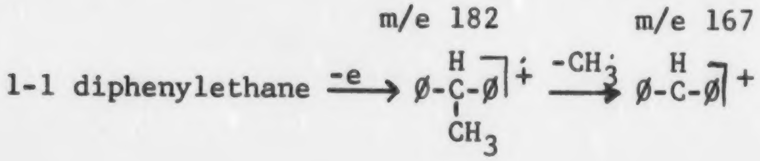
$$\mathrm{DDT} \xrightarrow{-e} \overset{m/e\ 352}{\left.\mathrm{Cl\emptyset\text{-}\overset{H}{\underset{CCl_3}{C}}\text{-}\emptyset Cl}\right]^{\dot{+}}} \xrightarrow{-CCl_3^{\cdot}} \overset{m/e\ 235}{\left.\mathrm{Cl\emptyset\text{-}\overset{H}{C}\text{-}\emptyset Cl}\right]^{+}}$$



$$\text{DDD} \xrightarrow{-e} \overset{\text{m/e }318}{\left.\mathrm{Cl\phi{-}\overset{H}{\underset{CHCl_2}{C}}{-}\phi Cl}\right]^{\dot{+}}} \xrightarrow{-\mathrm{CHCl_2^{\cdot}}} \overset{\text{m/e }235}{\left.\mathrm{Cl\phi{-}\overset{H}{C}{-}\phi Cl}\right]^{+}}$$

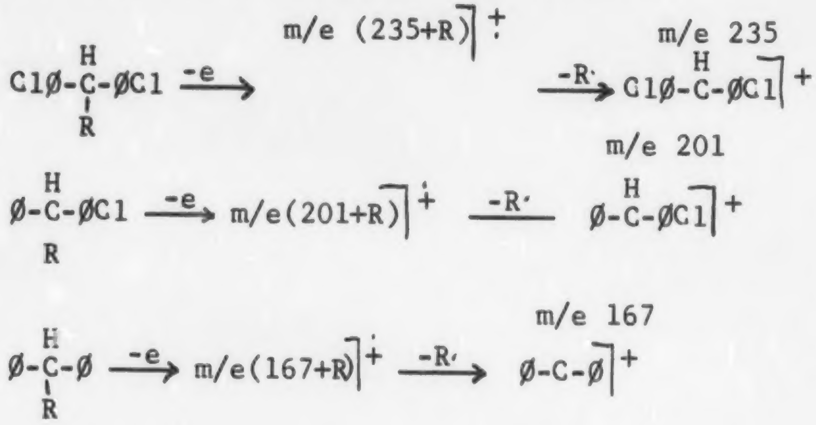
$$\text{DDMS} \xrightarrow{-e} \overset{\text{m/e }284}{\left.\mathrm{Cl\phi{-}\underset{CH_2Cl}{C}{-}\phi Cl}\right]^{\dot{+}}} \xrightarrow{-\mathrm{CH_2Cl^{\cdot}}} \overset{\text{m/e }235}{\left.\mathrm{Cl\phi{-}\overset{H}{C}{-}\phi Cl}\right]^{+}}$$

Similar behavior is also observed for the parent hydrocarbon



$$\text{1-1 diphenylethane} \xrightarrow{-e} \overset{\text{m/e }182}{\left.\mathrm{\phi{-}\overset{H}{\underset{CH_3}{C}}{-}\phi}\right]^{\dot{+}}} \xrightarrow{-\mathrm{CH_3^{\cdot}}} \overset{\text{m/e }167}{\left.\mathrm{\phi{-}\overset{H}{C}{-}\phi}\right]^{+}}$$

From this evidence it is reasonable to predict the following general behavior for reaction intermediates.

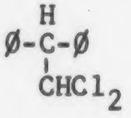


$$\mathrm{Cl\phi{-}\overset{H}{\underset{R}{C}}{-}\phi Cl} \xrightarrow{-e} \left.\text{m/e }(235+\mathrm{R})\right]^{\dot{+}} \xrightarrow{-\mathrm{R}^{\cdot}} \overset{\text{m/e }235}{\left.\mathrm{Cl\phi{-}\overset{H}{C}{-}\phi Cl}\right]^{+}}$$

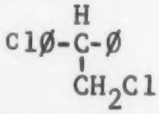
$$\mathrm{\phi{-}\overset{H}{\underset{R}{C}}{-}\phi Cl} \xrightarrow{-e} \left.\text{m/e}(201+\mathrm{R})\right]^{\dot{+}} \xrightarrow{-\mathrm{R}^{\cdot}} \overset{\text{m/e }201}{\left.\mathrm{\phi{-}\overset{H}{C}{-}\phi Cl}\right]^{+}}$$

$$\mathrm{\phi{-}\overset{H}{\underset{R}{C}}{-}\phi} \xrightarrow{-e} \left.\text{m/e}(167+\mathrm{R})\right]^{\dot{+}} \xrightarrow{-\mathrm{R}^{\cdot}} \overset{\text{m/e }167}{\left.\mathrm{\phi{-}C{-}\phi}\right]^{+}}$$

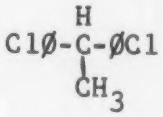
Such characteristic spectra were indeed observed. For example, Figure (5b-1) gives the observed mass spectra for the following three postulated structures:



$$\mathrm{\phi{-}\overset{H}{\underset{CHCl_2}{C}}{-}\phi}$$



$$\mathrm{Cl\phi{-}\overset{H}{\underset{CH_2Cl}{C}}{-}\phi}$$

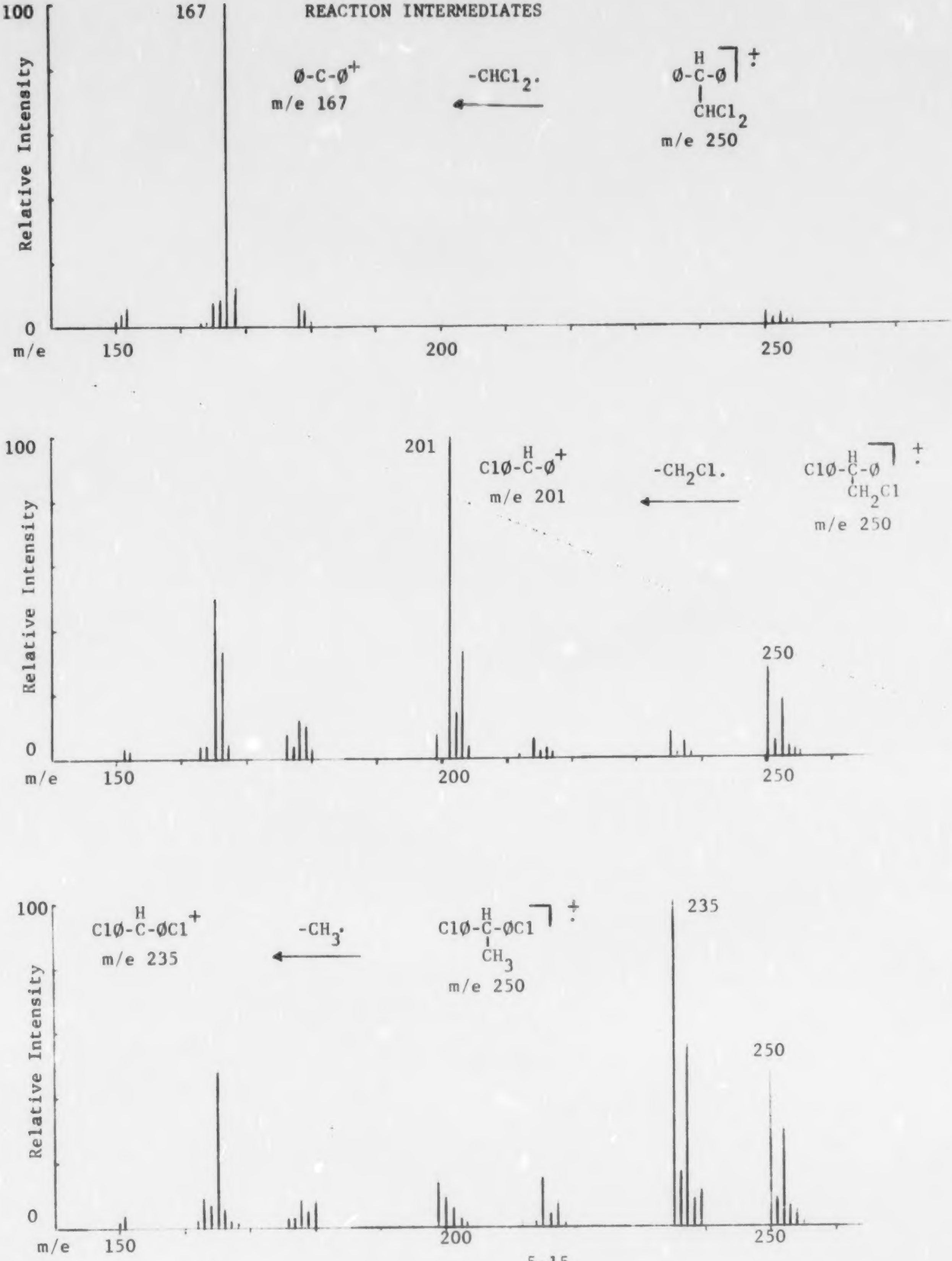


$$\mathrm{Cl\phi{-}\overset{H}{\underset{CH_3}{C}}{-}\phi Cl}$$

Figure (5b-1)

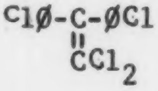
REPRESENTATIVE MASS SPECTRA OF DDE/DDD

REACTION INTERMEDIATES

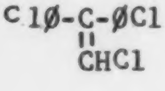


all with a molecular weight of 250 based on Cl^{35}. In all cases the major ion was formed by elimination of R·($CHCl_2$, CH_2Cl and CH_3 respectively) from the molecular ion.

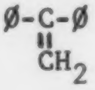
The mass spectra of chlorinated 1,1 - diphenylethylene reactants and products have been studied. Reference spectra were available from the literature (7,8) of the following three compounds:


$Cl\emptyset\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\emptyset Cl$

DDE


$Cl\emptyset\text{-}\underset{\underset{CHCl}{\|}}{C}\text{-}\emptyset Cl$

DDMU


$\emptyset\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}\emptyset$

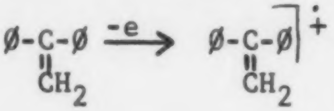
1,1-diphenylethylene

for the two polychlorinated compounds concerted removal of two chlorines from the molecular ion is observed which gives the major ion fragment

$$\mathrm{DDE} \xrightarrow{-e} m/e\ 316\rceil^{\dot{+}} \xrightarrow{-Cl_2} m/e\ 246\rceil^{+}$$

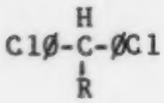
$$\mathrm{DDMU} \xrightarrow{-e} m/e\ 282\rceil^{\dot{+}} \xrightarrow{-Cl_2} m/e\ 212\rceil^{+}$$

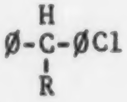
whereas with the parent hydrocarbon the major ion is the molecular ion itself.

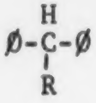

$$\emptyset\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}\emptyset \xrightarrow{-e} \emptyset\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}\emptyset\rceil^{\dot{+}}$$

In all cases fragmentation of the carbon skeleton across the olefinic bond does not characterize these spectra as with 1,1 - diphenylethanes.

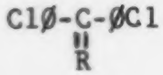
The mass spectra obtained of olefinic DDE reaction intermediator are not unambiguous. Intermediates containing the same number of chlorines/molecule be they olefinic, aromatic, or a mixture of both give similar mass spectra. However, chromatographic retention time data on the OV-17 column clarified identification to a great degree. Retention time data relative to PP' DDE obtained on a 9' x 1/8" 3% OV-17 on Chromasorb W-HP column, He 30 cc/min, 150 → 250°C @ 5°C/min. showed a consistent decrease in relative retention time of 0.22± .02 with removal of aromatic chlorine for each series of compounds

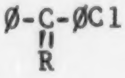

$Cl\emptyset\text{-}\underset{R}{\overset{H}{C}}\text{-}\emptyset Cl$

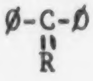

$\emptyset\text{-}\underset{R}{\overset{H}{C}}\text{-}\emptyset Cl$


$\emptyset\text{-}\underset{R}{\overset{H}{C}}\text{-}\emptyset$

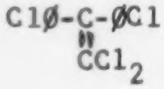
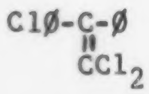
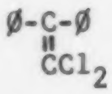
where R is $\overset{|}{C}Cl_3$, $\overset{|}{C}HCl_2$, $\overset{|}{C}H_2CL$, and $\overset{|}{C}H_3$. If this is true of the corresponding olefinic series


$Cl\emptyset\text{-}\underset{\overset{\|}{R}}{C}\text{-}\emptyset Cl$


$\emptyset\text{-}\underset{\overset{\|}{R}}{C}\text{-}\emptyset Cl$


$\emptyset\text{-}\underset{\overset{\|}{R}}{C}\text{-}\emptyset$

where R is $\overset{\|}{C}Cl_2$, $\overset{\|}{C}HCl$ and $\overset{\|}{C}H_2$ we should be able to predict the correct relative retention times for the olefinic series. Listed below are the predicted retention times for the series where R is CCl_2 and the observed retention time for olefinic intermediates as identified by GC/MS having the correct number of chlorines per molecule.

	Predicted R.T.	Observed R.T.
 $Cl\emptyset\text{-}\underset{\overset{\|}{C}Cl_2}{C}\text{-}\emptyset Cl$	N/A	1.000
 $Cl\emptyset\text{-}\underset{\overset{\|}{C}Cl_2}{C}\text{-}\emptyset$	0.78 ± .02	.79
 $\emptyset\text{-}\underset{\overset{\|}{C}Cl_2}{C}\text{-}\emptyset$	0.56 ± .02	.58

This good agreement shows the validity of the assumption for the olefinic series. In this way the whole series was identified except that the identity of 1 and 2 chloro olefinic compounds were ambiguous. Table 5b-1 lists relative retention time data and identification for all DDE/DDT series reactants and products, while Figure (5b-2) presents the data graphically.

Table (5b-1)

RELATIVE RETENTION TIME* DATA FOR 1,1 DIPHENYL ETHANES/ETHYLENES

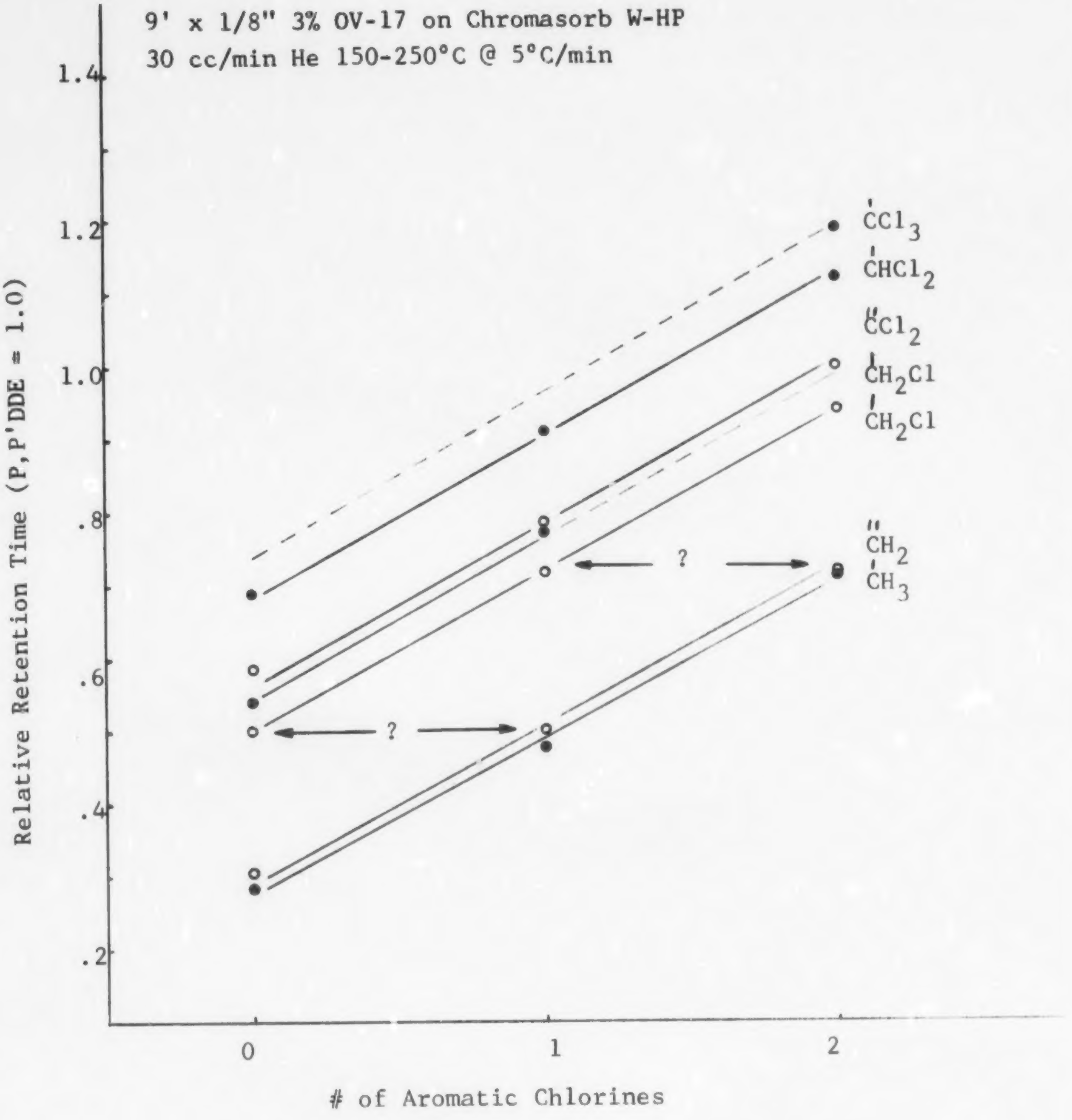
	$\overset{H}{\phi\text{-C-}\phi}$	$\overset{H}{\mathrm{Cl}\phi\text{-C-}\phi}$	$\overset{H}{\mathrm{Cl}\phi\text{-C-}\phi\mathrm{Cl}}$
$\overset{\vert}{\mathrm{C}}\mathrm{Cl}_3$			1.187
$\overset{\vert}{\mathrm{C}}\mathrm{HCl}_2$	.687	.910	1.120
$\overset{\vert}{\mathrm{C}}\mathrm{H}_2\mathrm{Cl}$	.542	.771	
$\overset{\vert}{\mathrm{C}}\mathrm{H}_3$	.283	.476	.711
	$\phi\text{-C-}\phi$	$\mathrm{Cl}\phi\text{-C-}\phi$	$\mathrm{Cl}\phi\text{-C-}\phi\mathrm{Cl}$
$\overset{\Vert}{\mathrm{C}}\mathrm{Cl}_2$	.584	.789	1.000
$\overset{\Vert}{\mathrm{C}}\mathrm{HCl}$	.500	.717	.940
$\overset{\Vert}{\mathrm{C}}\mathrm{H}_2$	.307	.500	.717

* Relative to PP' DDE @ 16.6 min

9' x 1/8" 3% OV-17 on chromasorb W-HP 30 cc/min H_e

150 — 250°C @ 5°C/min.

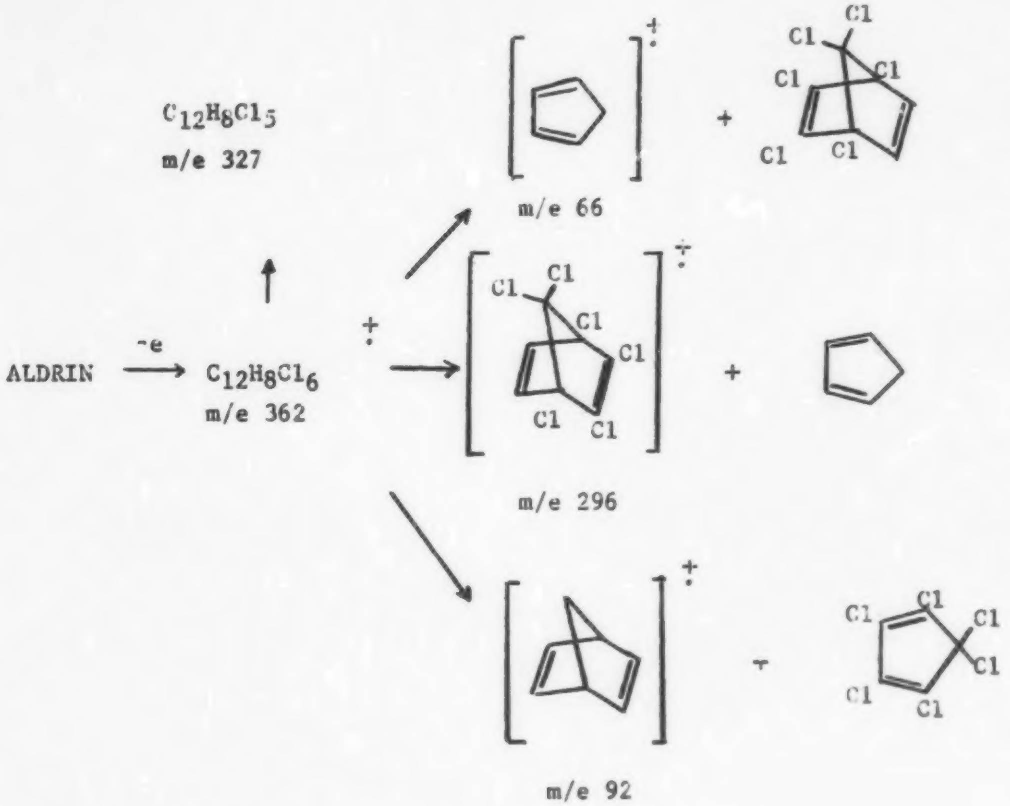
Figure (5b-2)
RELATIVE RETENTION TIMES OF DDT, DDE, DDD REACTANTS AND PRODUCTS

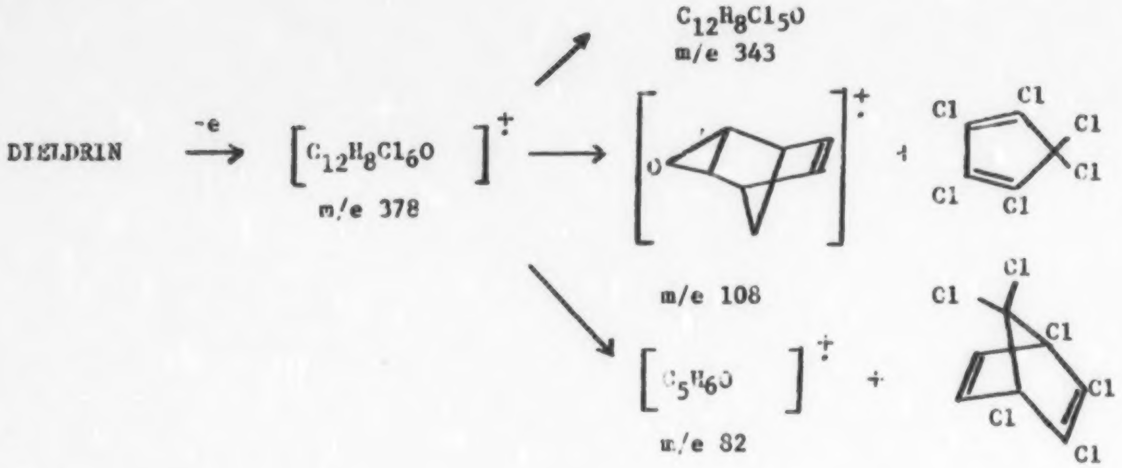


V-C ALDRIN DIELDRIN ANALYSIS

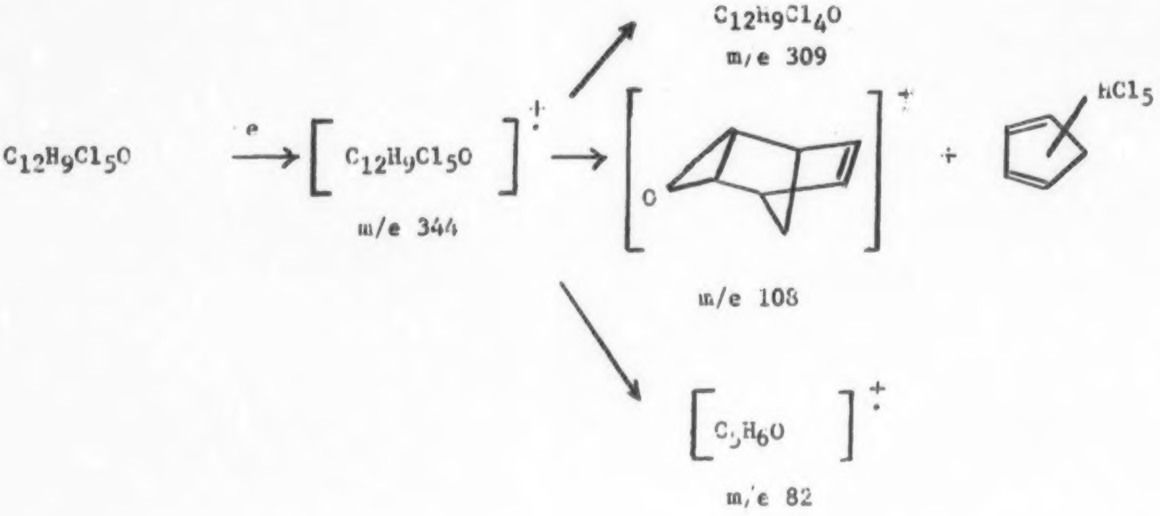
GC-MS Identification of Aldrin and Dieldrin and their hydrodechlorination products was carried out utilizing a 9' x 1/8" 3% OV-17 on Chromosorb W-HP column.

Safe and Hutzinger (6) have summarized the interpretation of electron impact (E.I.) mass spectra of Aldrin and Dieldrin. The fragmentation patterns of both compounds are characterized by retro Diels-Alder (RDA) reactions accompanied by or preceded by expulsion of Cl or HCl i.e.



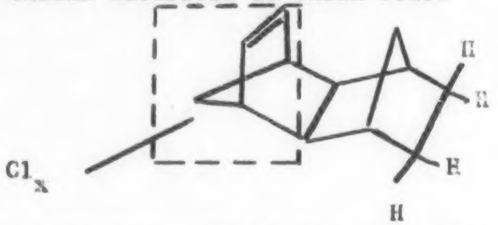


similar spectra were obtained for Dieldrin hydrodechlorination products where the olefin was not saturated e.g.



However since these spectra were characterized by RDA reactions no information could be obtained on which chlorine was removed during the hydrodechlorination process.

A series of mass spectra was also obtained on Aldrin hydrodechlorination products where one olefin had been saturated during reaction. Fragments due to RDA reactions were much less intense and the spectra were mainly characterized by elimination of chlorine from the molecular ion. This information plus the fact that initial hydrogenation of the corresponding epoxide Dieldrin was not observed, and obeservation from the DDE studies that hydrodechlorination is a precursor to olefinic hydrogenation, characterizes these intermediate as having the terminal olefin saturated as shown below



Retention time data, and MS identification of major reaction products were obtained except that the retention times of Aldrin, hydrogenated Aldrin and Dieldrin were virtually identical to the corresponding hydrodechlorination intermediates having 5 chlorine atoms per molecule.

Retention time data for Aldrin and Dieldrin products are found in Table (5c-1,2) respectively.

Table (5c-1)

RETENTION TIMES FOR MAJOR ALDRIN PRODUCTS

9' x 1/8" 3% OV-17 on chromosorb W-HP 102-250°C @ 8°C/min 30 cc/min He

R.T. (min)	MS IDENTIFICATION
10.6	$C_{12}H_{16}Cl_2$
14.1	$C_{12}H_{15}Cl_3$
15.1	$C_{12}H_{12}Cl_4$
15.6	$C_{12}H_8Cl_6$ (ALDRIN)
16.2	$C_{12}H_{11}Cl_5$
16.4	$C_{12}H_{10}Cl_6$

Table (5c-2)

RETENTION TIMES FOR MAJOR DIELDRIN PRODUCTS

9' x 1/8" 3% OV-17 on chromosorb W-HP 102-250°C @ 8°C/min 30 cc/min He

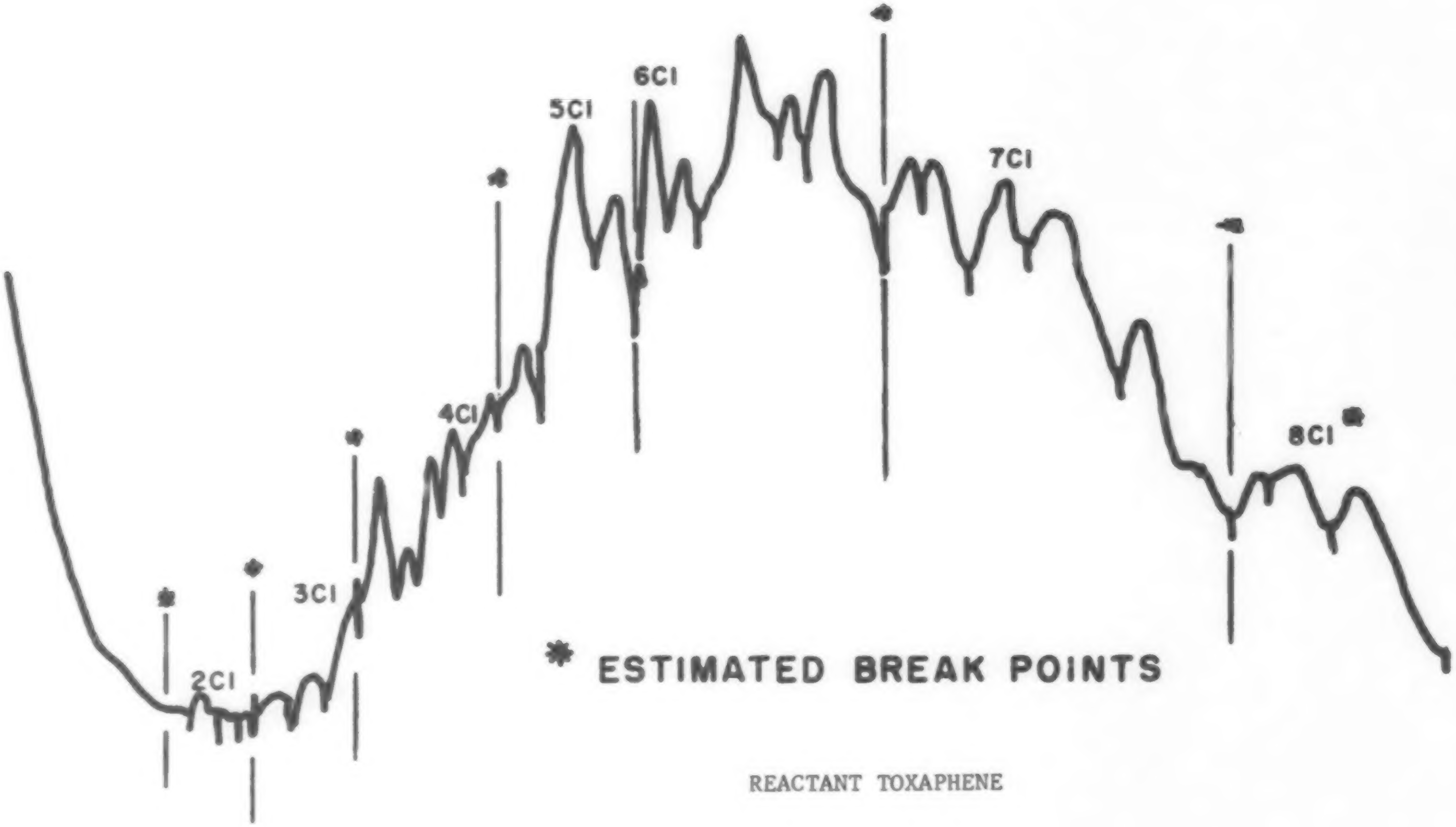
R.T. (min)	MS IDENTIFICATION
18.0	$C_{12}H_{10}Cl_4O$
18.4	$C_{12}H_8Cl_6O$ (DIELDRIN) + $C_{12}H_9Cl_5O$

V-D TOXAPHENE ANALYSIS

Toxaphene is a very complex mixture of polychlorinated comphene isomers (see section 3-D for details). As with other pesticides toxaphene and its reaction products were analyzed by GC-MS using both a 5'x 1/8" 3% OV-1 on Chromosorb W-HP column and a 9'x 1/8" 3% OV-17 on Chromosorb WHP colmn. Typical chromatograms of Toxaphene and its reaction products obtained using the OV-1 column are presented in figures (3D-1,2) respectively. These figures contain estimated break points between groups of isomers having the same number of chlorines / molecule. However based on area % calculations and representative mass spectra it was calculated that toxaphene contains an average of 6.15 chlorine atoms / molecule vs. 7.8 chlorines / molecule based on 68 wt.% chlorine as specified by the manufacturer (Hercules). Holmstead et al (9) have presented the mass spectra of two toxaphene components, one a $C_{10}H_{11}Cl_7$ compound and the other a $C_{10}H_{10}Cl_8$ compound. Their results show that for both compounds no molecular ions are observed in both CI and EI spectra but rather $M-Cl^+$ ions are the heaviest species observed. Weininger (10) has suggested that this behavior is due to the presence of perchlorinated carbon which readily loses one chlorine arom to form a stabilized carbonium ion. As these chlorines are replaced by hydrogen during reaction molecular ions should be observed and the accuracy of the analysis increased as chlorine conversion increases. Figure (3d-3) is a chromatogram of reaction products obtained on the OV-17 column with mass spectral identifications and estimated break points indicated.

Figure (5d-1)

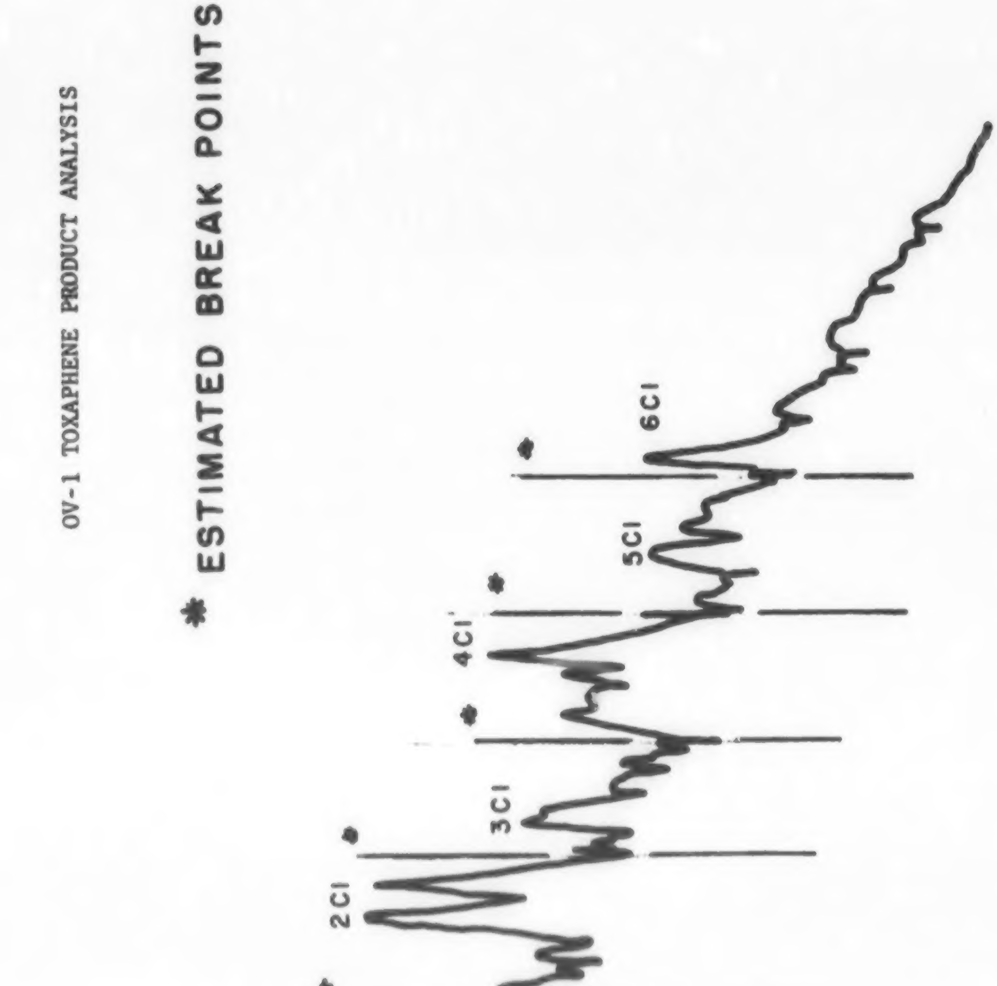
OV-1 TOXAPHENE ANALYSIS



REACTANT TOXAPHENE

Figure (5d-2)

OV-1 TOXAPHENE PRODUCT ANALYSIS

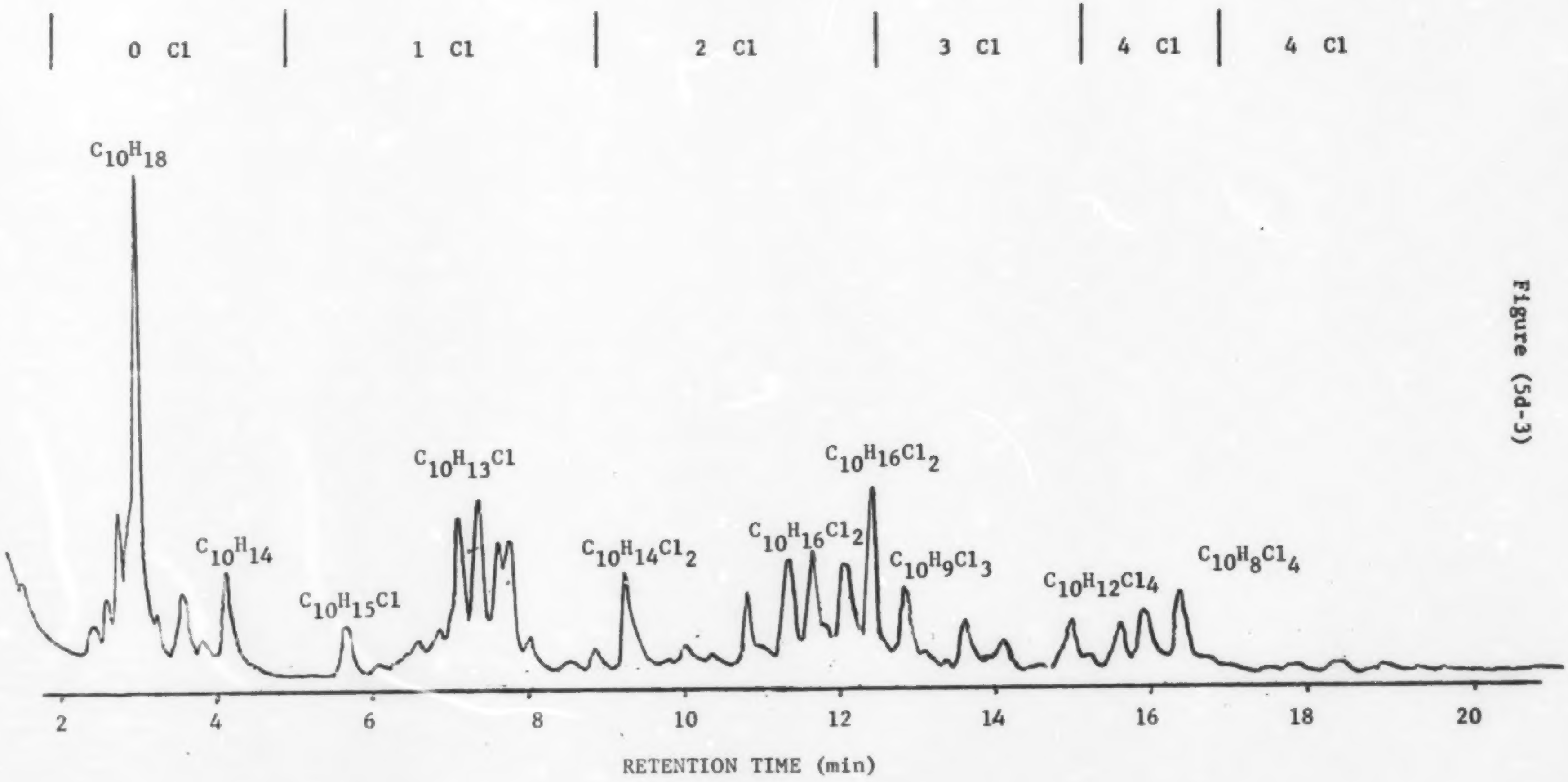


TOXAPHENE HYDRODECHLORINATION PRODUCTS

Figure (5d-3)

OV-17 GC-MS ANALYSIS OF TOXAPHENE HYDRODECHLORINATION PRODUCTS

9' x 1/8" 3% OV-17 on Chromosorb W-HP 82-250°C @ 8°C/min



V-E TOXICOLOGY

As a part of the program EPA arranged that toxicology of our starting materials and products be studied by the Toxicology Division, Biomedical Laboratory, Edgewood Arsenal. The program there was under the direction of Dr. B. P. McNamara with B. J. Brown in charge of the actual test work.

The test used by the toxicologists was mouse IV LD50. In this test a solution of the compound to be evaluated was injected (in different volumes) into the tail vein of white mice. The volume of solution (or weight of pesticide contained in the injected solution) per kilogram of mouse weight required to kill 50% of the mice injected is reported in Table (5e-1). Also reported is the 95% confidence range of this 50% lethal dose.

Data for Aroclor 1248 and its fully hydrodechlorinated derivative (diphenyl) dissolved as a 10% solution in hexane, show no significant difference in toxicity. In fact if the results are taken literally, diphenyl is slightly more toxic than the original aroclor. Interpretation is also obscured by the fact that the toxicity of both the aroclor and diphenyl is apparently about the same as that of the solvent hexane. This toxicity test is then not appropriate to distinguish between our starting materials and ordinary acceptable chemicals. The test shows gross short term poisoning.

The same is true of DDT tested as a 2.5% solution in dioxane. The original material, (DDT) was not distinguishable in toxicity from the fully hydrodechlorinated product (diphenyl ethane) or the solvent (dioxane). Gross quantities, 0.31-0.39 ml/kg doses of all materials act as poisons.

The tests described above were on samples whose concentration in solvent was accurately measured (Samples WPI-28 thru 35). In earlier, preliminary tests the concentration in solvent (propylene glycol or mineral oil) was only approximately known. Although the starting material and solvent were initially combined in equal weights, the processing resulted in considerable change in concentration as a result of refluxing and decomposition.

Results of these preliminary tests, on the assumption that concentrations remained at the initial 50%, show that the toxicity of toxaphene was reduced by a factor of about ten by hydrogenation in propylene glycol. Dieldrin toxicity was also reduced by a factor of ten or more. As in the later runs previously mentioned results of the early tests on Aroclor 1248 and DDT were inconclusive.

We do not recommend continued use of this test or literal interpretation of the toxicity results as an assessment of the environmental acceptibility of materials reacted in this study.

TABLE (5e-1)

TOXICOLOGICAL STUDIES OF COMPOUNDS PRODUCED BY

WORCESTER POLYTECHNIC INSTITUTE

Sample Number	Starting Material	Liquid Medium	CA $(OH)_2$ Treatment HRS	Hydrogenation with Ni Catalyst HRS	Mouse, iv LD50 (95% CL)
Reference	Aroclor				0.37(0.30-0.45) ml/kg
WPI - 1	"	none	none	(several)	0.65(0.63-0.68) ml/kg
WPI - 3	"	Propylene glycol	3	none	0.48(0.40-0.59) ml/kg
WPI - 2	"	" "	18	6	114.9(104.7-126.2) ml/kg (?)
WPI - 12*	"	" "	18	0	0.37(0.34-0.41) ml/kg
WPI - 13	"	" "	6	0	0.22(0.20-0.25) ml/kg
Reference	DDT				76.8(68.1-86.7) mg/kg
WPI - 5	"	Propylene glycol	12	6	194.4(155.5-243.0) mg/kg
WPI - 6	"	Mineral oil	12	0	1.0(0.95-1.05) ml/kg
WPI - 7	"	"	12	(several)	1.41(1.29-1.54) ml/kg
WPI - 8	"	Propylene glycol	16	0	0.071(0.064-0.079) ml/kg
WPI - 9	"	" "	3	6	199(164-242) mg/kg
WPI - 10	"	" "	6	6	162(144-182) mg/kg
WPI - 11	"	" "	6	0	351(320-384) mg/kg
WPI - 22	"	continuous hydrogenation of DDT in gas phase		During 1st 2 hrs	0.40(0.37-0.43) ml/kg
WPI - 23	"			During 2nd 2 hrs	0.79(0.73-0.86) ml/kg
WPI - 24	"			During 3rd 2 hrs	0.56(0.56-0.56) ml/kg
Refernece	Toxaphene				20.5(19.6-21.4) mg/kg
WPI - 14	"	Propylene glycol	12	6	0.39(0.33-0.45) ml/kg
WPI - 15	"	" "	3	0	0.14(0.12-0.16) ml/kg
Reference	Dieldrin				10.5(9.3-11.8) mg/kg
WPI - 16	"	Propylene glycol	6	6	0.29(0.26-0.32) ml/kg
WPI - 17	"	" "	16	6	0.35(0.31-0.40) ml/kg
WPI - 18	"	" "	6	0	0.11(0.10-0.14) ml/kg
WPI - 19	"	" "	3	0	0.40(0.37-0.43) ml/kg
WPI - 20	"	" "	16	0	0.30(0.27-0.33) ml/kg
WPI - 21	"	" "	3	6	138(127-150) mg/kg

TABLE (5e-1) cont.

TOXICOLOGICAL STUDIES OF COMPOUNDS PRODUCED BY

WORCESTER POLYTECHNIC INSTITUTE

Sample Number	Starting Material	Liquid Medium	Mouse iv LD50 (95% C.L.)
WPI - 32	Aroclor (10%)	Hexane	0.40(0.32-0.49) ml/kg
WPI - 30	(Ideal Product)	Hexane	0.27(0.24-0.30) ml/kg
	Pure Biphenyl - 10%		
WPI - 28	(Actual Product) 1st run (10%)	Hexane	0.23(0.20-0.26) ml/kg
WPI - 29	(Actual Product) 2nd run (10%)	Hexane	0.24(0.22-0.27) ml/kg
WPI - 33	Pure Hexane	-	0.27(0.24-0.31) ml/kg
WPI - 31	DDT (2.5%)	Dioxane	0.39(0.34-0.44) ml/kg
WPI - 36	(Ideal) Hydrodechlorinated DDT (Pure diphenyl ethane) (2.5%)	Dioxane	0.36(0.31-0.41) ml/kg
WPI - 35	Pure Dioxane	-	0.31(0.27-0.34) ml/kg

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4) Lao, R. C., Thomas, R. S., Monkman, J. L., and Pottie, R. F., Symp. on the Ident. and Meas. of Envir. Pollutants, Nat. Res. Council, Ottowa, Canada 144, 1971

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6) Safe, S., and Hutzinger, O., "Mass Spectroscopy of Pesticides and Pollutants, CRC Press, 18901 Cranwood Parkway, Cleveland, Ohio Copyright 1973

7) Bonelli, E. J., Taylor, P. A., and Morris, W. J., American Laboratory 29-35 July 1975

8) A.P.I. Research Project 44, Selected Mass Spectral Data Chem. Thermo. Properties Center. Texas A+M University, College Station, Texas

9) Holmstead, R. L., Khalifa, and Casida, J. E., J. Agr. Food Chem., Vol. 22, No. 6, 1974

10) Weininger, S. J., Interdepartmental Communication

VI SUMMARY & CONCLUSIONS

Prior to this study little was known about the hydrodechlorination of polychlorinated hydrocarbons, and more specifically hydrocarbons where combinations of aromatic, olefinic and aliphatic chlorine were bound to the same substrate.

This report not only establishes the hydrodechlorination stoiochometry of several polychlorinated pesticides and related substances but also includes the results of preliminary process variable (e.g. hydrogen pressure and temperature dependence) studies necessary to scale up the process.

Hydrodechlorination reactions may be carried out in several types of reactors each with their own advantages. A pulse microreactor interfaced with a GC-MS facility is a powerful tool in determining catalyst activity and reaction selectivity. This method allows for rapid determination of the reactivity of other classes of pesticides and related substances not studied here. A continuous gas phase reactor may be used for evaluating catalyst stability and is a possible process alternative under controlled conditions.

Liquid phase stirred autoclaves capable of being operated at elevated temperature and pressure may be used for obtaining kinetic data and associated reaction paths. These reactors are also the basis for the most feasible process alternative.

A large body of experimental data has been accumulated on the catalytic hydrodechlorination of several classes of pesticides and related substances using supported Ni and Pd catalysts. The major conclusions to be drawn from these data are as follows.

1) Inexpensive supported Ni catalysts, such as the 61% Ni on Kieselguhr used in these studies, are adequate for the hydrodechlorination of pesticides and related substances. Reactions catalyzed with 10% Pd on charcoal exhibited similar stoiochometry to those observed with Ni and the apparent activation energies observed during liquid phase DDE hydrodechlorination were virtually